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MINING AND MARKETING OF BARITE

BY

CHARLES L. HARNESS AND F. M. BARSIGIAN

I.C. 7345,
May 1946.

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

MINING AND MARKETING OF BARITE[1]

By Charles L. Harness[2] and F. M. Barsigian[3]

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[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7345."

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INTRODUCTION

The barite industry has made notable progress since the days when barite was used only as an adulterant in white-lead paints and the only method of mining it was with pick and shovel. The following chronological record may serve to show how this heavy white mineral has grown in importance in the national economy and at the same time to indicate development of methods for obtaining it.

1845. - Barite first mined in Fauquier County, Va., for use as an adulterant in white-lead paints.

1850 (approx.). - French settlers 60 miles southwest of St. Louis, Mo., discovered barite; called it "tiff", meaning white. It was mined and shipped to St. Louis for use in paint.

1860. - Price of Missouri barite was $7 a short ton, as shown by old ledgers.

1880. - Census recorded production of 4,425 short tons of barite in Missouri, 465 in Tennessee, and 4,575 in Virginia.

1892. - Second major outlet for barite: Lithopone industry began in the United States.

1901. - Production first reported in Georgia.

1903. - Production first reported in Kentucky.

1914. - Rollin Chemical Co. built barium chemical plant at South Charleston, W. Va., acquired by Barium Reduction Corp. in 1923.

1914-16. - First washers and jigs installed in Georgia and Tennessee.

1914. - Barite and witherite first mined near El Portal, Calif., by Barber Chemical Co. for manufacture of barium chemicals in San Francisco. (Not the same mine now worked by National Lead Co.).

1915. - Chicago Copper & Chemical Co., Blue Island, Ill., began making barium chemicals.

1915. - Precipitated barium carbonate first used as a substitute for ground bone meal in case carbonizing, as price of bone meal had risen to over $60 a ton.

1916. - Thompson-Weinman & Co. opened grinding plant at Cartersville, Ga.

1916. - Grasselli Chemical Co., Grasselli, N.J., began manufacture of barium chemicals.

1920. - The deposit at El Portal, Calif., now operated by National Lead Co., first worked by another producer.

1923-24. - First washer installed in Missouri.

1926. - Third major market for barite: Stroud patented its use as a mud weight in rotary well drilling, and National Pigments & Chemical Co. (now National Lead Co.) put "Baroid" (ground barite for well drilling) on the market.

1928. - First use of barite as a flux in window and container glass.

1929. - Great Western Sugar Co., Denver, Colo., first produced barium hydroxide from witherite for use in sugar refining.

1934. - Price of barite in Missouri fell to $1.50 a short ton, too low to permit competition of washers with hand miners.

1941. - Magnet Cove Barium Co., Malvern, Ark., separated ground barite from associated minerals by flotation.

DESCRIPTION

Barite varies widely in appearance in various parts of the United States. In Washington County, Missouri, and in Tennessee and Georgia it takes the shape of white abraded nodules, commonly stained with iron oxide, ranging from microscopic size to 8 inches or larger. Most of the pieces appear to be smaller than fist size. Recognizable orthorhombic crystals are mined commercially from time to time near Jefferson City, Mo. Massive Nevada barite is generally gray. That mined at El Portal, Calif., is white. Barite from Nevada County, Calif., is marketed in the form of white lumps with iron stains. Arkansas crude barite has replaced shale with a varvelike effect of alternating thin (about 1/8 to 1/16 inch) brown and white layers. The distinguishing feature of the mineral, wherever found, is its high specific gravity, 4.5. A piece of barite fuses at its thin edges with a yellow-green flame when held in the blowpipe flame. Celestite, another heavy (sp. gr. 3.96) white mineral sometimes mistaken for barite, gives a crimson flame. The reported hardness of barite is 3 (Mohs' scale). However, there seems to be some variation in Missouri and Eastern barites in the ease with which the material can be crushed and ground, and the former is preferred for grinding because it is softer.

In Georgia and Tennessee barite is called barytes (pronounced bear-i-tease, accent on first syllable, the "i" short); in Missouri, tiff; and in Nevada and California, barite.

Barite is theoretically 65.7 percent BaO and 34.3 percent SO_3. However, impurities of iron, silica, strontium, calcium, magnesium, and other materials are nearly always present. Minimum permissible impurities are discussed under Specifications. Chemical-grade barite is generally sold on a basis of 94 percent barium sulfate minimum and 1 percent iron oxide maximum.

OCCURRENCES

Roughly speaking, there are two commercial types of occurrence: (1) Residual, where lumps of barite remain as a result of weathering of barium-bearing rocks, chiefly dolomites in Missouri and the Eastern States; and (2) total or partial replacement in shale or limestone, such as the deposits near Magnet Cove, Ark., in northern Nevada, in Cocke County, Tenn., at El Portal, Calif., and other areas. Barite can rarely be recovered commercially as a gangue of metal mining, although this has been tried in a few instances, nor has it so far been separated commercially from fluor-barite. Deposits are discussed by States in the following pages.

Arkansas

Barite was discovered accidentally in drilling a water well on the northern slope of Chamberlin Creek Valley in 1900.[4] About 100 acres of this area (15 miles east of Hot Spring) is underlain with barite, and reserves, as yet incompletely mapped, are estimated at several million tons. Little exploratory work was done until about 1930, and sustained production was begun only in 1941 by the Magnet Cove Barium Corp. The two present workings of the National Lead Co. and the Magnet Cove Barium Corp. are on opposite converging wings of a bedded synclinal deposit. The barite bed occurs as a replacement of Stanley shale of Pennsylvanian age, and the width of the minable zone ranges from 30 to 70 feet. The rock varies in color and may be red, yellow, gray, or green. Analyses are variable and may range from 50 to 70 percent barium sulfate, the gangue consisting chiefly of silicates of iron and aluminum. The original average analysis of 86 percent barium sulfate obtained by Parks has not been borne out in practice.

The Magnet Cove area is named after an elliptical igneous intrusion lying 2 miles west of the open cuts. This intrusion is believed to be the source of the barium, which is presumed to have been carried by hydrothermal solutions along porous zones in the shale, replacing shale and depositing in pores. Barite from this area has no commercial value in its impure state and must be beneficiated for use.

Missouri

It is generally agreed that the barite in the residual deposits in Missouri is "the result of the accumulation and concentration of the barite originally deposited in veins and cavities of the overlying strata released by solution and weathering of the more soluble rock minerals, mainly calcium and magnesium carbonates, of which these rocks were composed. The clays are also the result of this action, making conditions proper for the formation of the ore bodies when not subjected to erosive action."[5]

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[4] Parks, B., A Barite Deposit in Hot Spring County, Ark.: Arkansas Geol. Survey Inf. Circ. 1, 1932, 52 pp.

[5] Weigel, W. M., The Barite Industry in Missouri: Am. Inst. Min. and Met. Eng. Tech. Pub. 201, February 1929, p. 13.

This theory is applicable to both the Washington County and the Central districts. There is considerable dispute, however, as to how the barite entered the dolomite in the first place, i. e., whether from ascending or descending waters. Bracciations of the limestone caused by dolomitization were thought by writers[6] of a generation ago to have been filled with barite from magmatic waters. Later work seems to indicate that the fissures resulting from dolomitization were filled by surface waters.

In the Washington County and Central areas the following formations have been identified:[7]

Lower Ordovician:
- Jefferson City
- Roubidoux
- Gasconade

Cambrian:
- Proctor
- Eminence
- Potosi
- Derby-Doe Run
- Davis
- Bonne Terre
- Lamotte sandstone

In the Washington County area, residual clay from the Potosi formation is the most important source of barite. Less important are clays from the Eminence, which outcrops in the western part of the district. The Proctor and Gasconade are not sources of barite in the Washington County district, though the Gasconade is important in central Missouri. The Potosi formation is distinguished from the Proctor, Eminence, and other dolomite formations of the area because of its considerable content of drusy quartz and chalcedony.[8] The Washington County area includes about 230 square miles, according to Tarr, comprising all townships of 37 N., R. 2 and 3 E.; 38 N., R. 2 and 3 E.; 39 N., R. 3 E.; the southern part of T. 40 N., R. 3 E.; nearly half of T. 39 N., R. 3 E.; and the southwest sections and the northwest corner of T. 39 N., R. 4 E. According to Weigel,[9] the Washington County field is limited to the east and north by intersecting faults striking respectively northwest (downthrow on northeast side) and northeast (downthrow on northwest side).

Barite is generally concentrated in the residual clay at certain depths, and at these depths the larger pieces are generally found in "leads" a few feet wide and up to several hundred feet long. These leads were conscientiously followed by the hand miners and are today mined first in modern power-shovel recovery. Vertically, a typical section of the soil is:[10]

6/ Steel, A. A., The Geology and Preparation of Barite in Washington County, Mo.: Bull., Am. Inst. Min. and Met. Eng. No. 38, February 1910, pp. 85-117.
7/ See footnote 5.
8/ Tarr, N. A., Barite Deposits of Missouri: University of Missouri Studies, vol. 3, No. 1, 1918, p. 27.
9/ See footnote 5.
10/ See footnote 5.

	Thickness, feet
Surface soil	1-1½
Chert, gravel, and clay	1½-2
Clay and small (minus 2 inches) fragments of chert, quartz, and barite	2½-4
Virtually barren dark-red clay	3-4
Red clay, large chert, dolomite boulders, and large masses of barite, sometimes in almost continuous sheets 4 to 6 inches thick and several square feet horizontal extent	1-2½
Red clay	To bed rock

Both mechanical and chemical changes enter into the weathering of dolomite. Weathering induced by freezing probably is the most active agent down to the frost line, and from there through the porous zone of the dolomite meteoric water is the effective means of weathering. Quartz and barite remain because of their extreme insolubility. (One part of barite dissolves in 435,000 parts of water.) Dolomite is dissolved partly because it is slightly soluble in water but mostly because it reacts chemically with carbonate ions in the water, yielding calcium and magnesium bicarbonates in solution. Thus, circulation of water is necessary to weather away dolomite; but if the gradient is too steep, the residual soil with its barite content is carried away as it is made. Therefore, gentle slopes favor the accumulation of barite, and it is said that the best fields are found on such slopes.[11]

Although barite in the Central district, near Jefferson City, occurs through the weathering of dolomite (Gasconade formation) just as in the Potosi formation in Washington County, the only commercial occurrences are found in "circles", hillside caves in dolomite filled with residual clay, barite, and chert. The caves, which may have a diameter up to about 300 feet, are worked by power shovels and log washers just as in Washington County. Most of the museum-grade crystals of Missouri barite come from these "circles."

Georgia

Barite is now being mined only in the Cartersville district in Bartow County, where there are many closely adjacent deposits. There are also a few deposits in Polk, Floyd, Cherokee, Gordon, Murray, and Whitfield Counties, but none of them have been mined for a considerable time.

The geologic occurrence of barite in the Cartersville district is summarized as follows from descriptions by Hull[12] and Kesler[13]: The Cartersville deposits occur in clays derived from the weathering of lower Cambrian dolomite. The barite contains various sulfides in very small amounts. A few pinnacles of the dolomite, which contain veins and replacement bodies of the barite, indicate that all of the barite in the clay has been freed from dolomite during the process of weathering. Details of geologic structure show that the deposition of barite in the dolomite occurred in and adjacent to fault zones, and it is inferred that the deposition was effected by hot solutions derived from great depth in late Paleozoic time. The economically important deposits of barytic clay have been formed by subsequent weathering.

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[11] See pp. 71-72 of footnote 8.

[12] Hull, J.P.D., Report on the Barytes Deposits of Georgia: Georgia Geol. Survey Bull. 36, 1920, 146 pp.

[13] Kesler, T. L., Structure and Ore Deposition at Cartersville, Ga.: Am. Inst. Min. and Met. Eng. Tech. Pub. 1226, 1941, 18 pp.

Tennessee

At this writing barite is mined at only two places in Tennessee - near Sweetwater and in Cocke County. The former is the more important, supplying considerable quantities of glass- and chemical-grade barite. The latter furnishes a filler-grade material. Other areas, active in the past, include the Pall Mall district about 10 miles north of Jamestown, the Falls Branch district about 10 miles south of Kingsport, the Lost Creek district near Sharps Chapel in Union County, and others.

In the Sweetwater district barite occurs in residual clay from the weathering of Knox (Cambro-Ordovician) dolomite in three separate parallel zones. Barite occurring in the dolomite itself has no commercial importance. These zones or veins are known as the Howard, 3 miles southeast of Sweetwater, and the Garrison, and Culveyhouse, 4 and 6 miles, respectively, northwest of Sweetwater. The zones are usually 100 to 300 feet wide and 60 to 80 feet deep. The distance between terminal workings on the three veins ranges from about 9 to about 17 miles. Workable deposits, however, appear only at intervals. Chert, iron oxide, and fluorspar are the chief associated impurities. As evidenced by banded pieces of barite found in the area, calcite, pyrite, fluorite, and barite were deposited in fissures in that order. In weathering, the calcite was largely dissolved and the pyrite oxidized to limonite. Fluorite, being relatively insoluble, remained unaltered.[14] Only the veins in which the original deposition of fluorspar was negligible have weathered to yield commercial-grade barite.

Chert is removed in jigging, but iron oxide and fluorite are generally present as crusts and remain attached to the barite. The iron is separable to some extent by crushing and magnetic separation, but when fluorspar is encountered the deposit is generally abandoned, for even a trace of fluorspar reported in an analysis is sufficient to disqualify that barite for chemical or lithopone use.

Gordon[15] believes that the source of the barite was in the Knox dolomite and that the small percentage of barium sulfate originally present in the dolomite was dissolved by descending waters and deposited in the bedded veins or shattered zones.

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[14] Laurence, R. A., Origin of the Sweetwater, Tenn., Barite Deposits: Econ. Geol., vol. 34, No. 2, March-April 1939, pp. 190-199.

[15] Gordon, C. H., Barite Deposits of the Sweetwater District, East Tennessee: Tennessee Geol. Survey, Resources of Tenn., vol. 8, No. 1, 1918, p. 56.

In the Pall Mall district of Fentress County, 10 or 11 miles north-northwest of Jamestown, barite occurs in residual red clays derived from underlying Mississippian limestones.[16] The barite-bearing clay outcrops for about a mile and is 1,000 feet wide and up to 15 feet thick. The Wolf River Corp. worked in this zone for several years, but mapped-out reserves were exhausted by the end of 1943.

Barite also occurs near Donelson in Davidson County; near Liberty, Dekalb County; near Charlotte, Dickson County; near Carthage, Smith County; at several places in Trousdale County; and in Wilson County.[17]

Cocke County furnishes the only barite other than that mined near Sweetwater. Here it occurs chiefly around Del Rio and Burnett, stations on the Ashville-Morristown, Tenn., branch of the Southern Railroad, which parallels French Broad River for some miles. This region is underlain by sedimentary rocks of Cambrian age, mostly sandstones, conglomerates, and shales metamorphosed into quartzites and slates.[18] The barite deposits occur in irregular fissures and as replacements in the rocks. The Clinchfield Sand & Feldspar Corp. is mining (1945) barite near Burnett in the Krebs (formerly called the Burnett) mine and in the Williams mine, formerly called the Minns mine. The following information on these mines has been furnished by B. S. Bonebrake, of the Clinchfield Sand & Feldspar Corp., in a letter to the senior author dated Jan. 1, 1945.

> Krebs mine. - The ore lies in the bedding of the country rock and has replaced shaly seams which alternate with more massive unreplaced sandstone beds. The ore zone runs through a thickness of 100 feet, and about one-half of this appears to be ore though possibly running as low as one-quarter. The ore occurs near the surface over many acres. The rocks lie about N. 70° E. and dip 20° to 25° southeast. The rocks are much jointed, and underground mining is difficult.
>
> Williams mine. - The veins developed at this mine are solid. The hanging wall is especially solid, standing without support in spaces up to 40 feet. The vein lies with a strike of N. 82° W. and a dip of 33° south. It varies in thickness from 6 to 14 feet, which thickness is maintained to a depth of 70 feet, being the present depth to which the veins have been worked.
>
> Analyses:

	Krebs	Williams
Moisture at 100° C............	0.08	0.10
Silica........................	24.48	11.48
Iron oxide....................	0.07	0.16
Barium sulfate................	62.80	71.00
Calcium fluoride..............	2.89	12.54.

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[16] Whitlach, G. I., Barite: Tennessee Dept. Conservation, Div. of Geol., Market Circ. 7, 2d ed., April 1938, p. 15.

[17] See pp. 15-17 of footnote 16.

[18] Gordon, C. H., Barite Deposits in Upper East Tennessee: Tennessee Geol. Survey Bull. 23, 1920, p. 65.

The material is used for filler purposes, for which the high silica and calcium fluoride content is not deleterious.

The deposits in Greene County are in residual clays from breccia veins in Knox dolomite, and intermittent shipments from this area have been made since as early as 1874, or perhaps even earlier.[19]

Two informative references not yet mentioned are given in the footnote.[20]

California

Bradley[21] has compiled considerable material on barite occurrences and preparation in California. The reader is referred to that work for descriptions of several deposits not included here.

Barite is being produced at two places in California in 1945 - one a mile west of El Portal, Mariposa County, operated by the National Lead Co., the other near Washington, Nevada County, operated by the Industrial Minerals & Chemical Co. Fitch[22] found that the group of barite-witherite veins arose by replacement of a bed of limestone constituting part of an isoclinally folded series of Paleozoic sediments. There are three veins, two of which are cut by the Merced River approximately at right angles to its general east-west course. The veins, which have been traced for about a mile north of the river and two miles south, are up to 20 feet wide, and the enclosing strata dip at about 80°. Fitch's work indicates that the calcite was replaced by barite and witherite and that some of the witherite was replaced by barite following oxidation of pyrite. At one time witherite was mined north of the Merced River. Present workings are south of the river, where witherite and barite occur together and are mined and processed together.

In the Spanish mine operated by the Industrial Minerals & Chemical Co. 2 miles north of Washington, Nevada County, barite occurs as a lens in a recently abandoned gold mine. Geologic data on this particular deposit are meager; the mining process is discussed on p. 18 .

Other California barite deposits occur in Inyo, Los Angeles, Nevada, Orange, San Bernardino, and Santa Barbara Counties.

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[19] Killebrew, J. B., Introduction to the Resources of Tennessee 1874, p. 617.

[20] Henegar, H. B., Barite Deposits in the Sweetwater District, Tennessee, Resources of Tennessee: Tennessee State Geol. Survey, vol. 2, Nov. 1912, pp. 424-29.
Penhallegon, W. J., Barite in the Tennessee Valley Region: T V A Geologic Bull. 9, 1938, 47 pp.

[21] Bradley, W. W., Mining in California.: Vol. 26, No. 1, January 1930. pp. 45-57.

[22] Fitch, A. A., Barite and Witherite from near El Portal, Mariposa County, California: Am. Mineral., vol. 16, No. 10 October 1931, pp. 461-68.

Nevada

One of the best references on barite deposits in Nevada is that prepared by Gianella.[23] Mention of barite mines in Eureka and Lander Counties is also made in Vanderburg's reconnaissance papers.[24] Three mines are producing barite: Barium King, operated by California-Nevada Barytes Mines, 4 miles southeast of Southern Pacific Railroad's Argenta siding; Pleasant View, operated by Barium Products, Ltd., 14 miles southeast of Battle Mountain; and a mine near Carlin.

Barite in the Battle Mountain (or Argenta) area occurs at the northwest extremity of the Shoshone Range. It is dark-gray and contains occasional chert nodules and some narrow bands of shale. The country rock is limestone and shale with some quartzite and conglomerate, and barite has replaced beds of gray limestone. The mine near Carlin consists of a 10-foot vein striking N. 30° W. and dipping 70° E. It is opened by adits and mined by open stopes.

Virginia

Barite has been mined in Virginia from both residual (clay matrix) and underground deposits in country rock. The former are the more important, and washer production from residual deposits in Campbell and Pittsylvania Counties has furnished most of the barite mined in Virginia since World War I. Residual deposits and prospects are also located in Fauquier, Roanoke, Botetourt, Russell, Tazewell, and Smyth Counties. Vein and breccia deposits have been found in Bedford and Grayson Counties. For details the reader is referred to Edmundson's review.[25]

Available evidence indicates that the original veins, replacements, and breccias were formed by rising aqueous solutions of magmatic origin. Weathering produced the familiar residual type of deposit. The deposits occur for the most part in Beekmantown limestone and dolomite.

The Campbell-Pittsylvania Counties barite belt extends from the Carson mine about 6 miles southeast of Lynchburg, southwestward to Pigg River, a distance of approximately 35 miles. Along this belt, numerous openings have been made, but those extensively worked are a few miles southeast of Evington and Toshes, respectively. The deposits are found in clay residual from marble. As late as 1942 the Barium Reduction Corp. operated a washer near Toshes, shipping from Gretna on the Southern Railroad.

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[23] Gianella, V. P., Barite Deposits of Northern Nevada: Am. Inst. Min. and Met. Eng. Tech. Pub. 1200, July 1940, 6 pp.

[24] Vanderburg, W. O., Reconnaissance of Mining Districts in Eureka County, Nevada: Bureau of Mines Inf. Circ. 7022, 1939, p. 64. Also, Reconnaissance of Mining Districts in Lander County, Nevada: Bureau of Mines Inf. Circ. 7043, 1939, pp. 53-54; 79.

[25] Edmundson, R. S., Barite Deposits in Virginia: Virginia Geol. Survey Bull. 53, 1938, 85 pp.

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Virginia appears to have been the first commercial source of barite in the United States. Watson[26] reports that a small deposit was operated in 1845 in Fauquier County. During this early period, Virginia seems to have been the chief producer, having been surpassed by Missouri in the 1890's.

North Carolina

Barite has been mined in two areas in North Carolina - in the Hot Springs area in Madison County and in the Kings Mountain area in Gaston County.

The Hot Springs area begins near Bluff, some 6 miles south of Hot Springs, and continues northeast by Stackhouse, a total length of 7 miles. This locality has not been active since 1925. The barite occurs as veins in fractured Archean granites and to some extent in feldspathic Cambrian quartzites, and is said to be derived from magmatic waters.[27]

The principal mines in the area are the Stackhouse, Washburn, Betts, and Gahagan. Topography is mountainous, and openings are 500 to 800 feet above the streams. The Stackhouse shaft is 500 feet deep; the others are less than 300 feet. Veins average 2 to 4 feet in width, except in the Stackhouse mine, where a maximum of 18 feet is reported. Much fluorite and quartz is interspersed with the barite, and considerable hand picking may be required to yield a merchantable product.

In the Kings Mountain area, barite occurs as veins in siliceous sericite schist of Algonkian age. The veins range in width from a few inches to 6 feet and consist of massive granules of barite ranging in color from pink and yellow to white. One of the most important properties in North Carolina, the Lawson mine, located on two exposed veins, is developed by numerous shafts and pits from 30 to 100 feet deep. The Kings Mountain area is an extension of the Kings Creek, S. C., barite occurrence, mined from time to time by Clinchfield Sand & Feldspar Co. of Baltimore.

Kentucky

Barite was first mined in Kentucky in 1903, when shipments were made from the Ray and Lowery mines in the western and from Scott County mines in the central part of the State. No barite has been produced in Kentucky since 1926.

The main occurrences are in central Kentucky. Leaner deposits are found in western and other areas of the State. The Central district comprises the Counties of Anderson, Bourbon, Boyle, Clark, Fayette, Franklin, Garrard, Harrison, Henry, Jessamine, Lincoln, Madison, Mercer, Owen, Scott, and Woodford. Other counties in which barite is said to occur are Russel, Cumberland, Caldwell, Christian, Crittenden, Livingston, Lyon, Trigg, Casey, Clinton, Grant, Estill, and Lincoln.

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[26] Watson, T. L., Geology of the Virginia Barite Deposits: Am. Inst. Min. and Met. Eng. Trans. vol. 38, 1907, pp. 710-733.

[27] Stuckey, J. L., and Davis, H. T., Barite Deposits in North Carolina: Am. Inst. Min. and Met. Eng. Contrib. 19, 1933, 9 pp.

Deposits in the Central district occur as veins in Ordovician limestone and as fragments in its clay residue. The veins are generally vertical deposits, which fade out or swell in their course along the dip or strike.[28]

They may reach a depth of over 1,200 feet, a length of 4 or 5 miles, and a width of 16 feet. Average depth is 600 feet and average width 2 to 4 feet. The veins are of the fissure, breccia, or replacement types or a combination of these. Impurities are calcite, fluorite, pyrite, galena, zinc blende, and marcasite. The chief impurity in the Athens region is said to be fluorspar, lead and zinc in the Georgetown-Lexington region, calcite with lead and zinc in the Gratz region, fluorite and calcite in the Harrodsburg-Wilmore region, zinc blende in the Danville region, and zinc and lead in the Paris-Millersburg region.

Mining was done chiefly by open cuts. There were few shafts or adits. The cuts were shallow, generally less than 15 feet deep. Overburden was removed by pick and shovel or steel scrapers. The material, hand-sorted in the cut and on the surface, was sized through a 1-inch screen. Plus one-inch was hand-cobbed, whereas the minus 1-inch went to the log washer for separation of clay and sometimes was crushed and jigged to remove galena, limestone, and silica.

Alabama

Sustained commercial production of barite in Alabama began in 1914 and ended about 1924. All output has been from residual deposits in red clay, somewhat similar to the sink hole deposits ("circles") in central Missouri. The clay is residual from Cambro-Ordovician limestones. Recent work[29] indicates the deposits to be of mesothermal and epithermal origin and that the barium was brought up in emanations from magmas and deposited as veins and replacements which were formed after the main Appalachian structure was developed at the close of the Paleozoic. The major barite districts in Alabama, according to Adams and Jones, are:

Bibb County, 6 to 10 miles north of Centerville.

Shelby County, Longview-Saginaw (southern part of county) and Vincent-Harpersville-Wilsonville (in eastern part).

Jefferson County, 3½ miles southwest of Leeds.

St. Clair County, Beaver Creek valley, east of Ashville.

Etowah County, Greens Creek Valley, on the southern border of the county.

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[28] Fohs, F. J., Barytes Deposits of Kentucky: Kentucky Geol. Survey, ser. 4, vol. 1, Pt. 1, 1913, pp. 441-585, at p. 456. (This is the basic reference on Kentucky barite.)

[29] Adams, G. I., and Jones, W. B.: Barite Deposits of Alabama: Alabama Geol. Survey, Bull. 45, 1940, 38 pp. at p. 16.

Calhoun County, near Angel station in northwestern part of county.

Cleburne County, about 6 miles south of Heflin.

Cherokee County, in southeastern corner of county, near Georgia-Alabama State line.

Most of the output has been from Calhoun, Bibb, and Shelby Counties.

The literature on Alabama barite indicates that the deposits are by no means exhausted, and perhaps the fields may be reopened at some future date. Additional references are given in the footnote.30/

South Carolina

The earliest report of production in South Carolina is in Mineral Resources of the United States for 1891. Since that time there has been intermittent production from lenticular veins in quartz sericite schist near Kings Creek, S. C., on the Southern Railroad. Vein content is chiefly massive granular barite varying in color from pure white to deep rose pink. Quartz veinlets and galena are easily separable impurities. Barite veins range in thickness from a few inches up to 8 feet or more and conform roughly to the strike and dip of the enclosing schist. In general, the strike is N. 25° E. and the dip 10° to 45°. "Ore" is mined by stripping the veins in open cuts and blasting out the barite. Galena is removed by hand sorting and the quartz by jigs.

Other States

States other than those already mentioned have never been important sources of barite. The following areas may be noted, however.

A small quantity of barite was shipped in 1915 from a deposit on the west coast of Prince of Wales Island, Alaska. Country rock is white limestone interbedded with talc schist. The barite body is tabular in shape, nearly vertical, and about 30 feet wide. The barite appears to be a replacement of the limestone. Analysis in percents: SiO_2, 0.42; iron oxides and Al_2O_3, 0.12; MgO, 0.16; CaO, none; SO_3, 34.01; BaO, 64.94; and SrO, none; equivalent barium sulfate, 98.9.31/

The principal locality in which barite was mined in Connecticut is at Cheshire, 10 to 12 miles north of New Haven, where it occurs as lenslike veins 2 to 4 feet wide.32/ There has been no output for 50 or 60 years.

30/ Jones, W. B., and McVay, T. N., Barite Deposits of the Sinks District, Bibb County, Alabama; Econ. Geol., vol. 29, No. 8, Dec. 1934, pp. 761-766.

Adams, G. I., Hydrothermal Origin of the Barite in Alabama: Econ. Geol., vol. 26, No. 7 November 1931, pp. 772-776.

31/ Geol. Survey, Mineral Resources of the United States, 1915, Part II, Nonmetals, p. 169.

32/ Geol. Survey, Mineral Resources of the United States, 1915, Part II, Nonmetals, p. 170.

A small output has been reported in Blaine County, Idaho, 9 miles northwest of Hailey, where crystalline barite occurs in lenticular masses,[33] and at Troy, Lincoln County.

A small output of barite from residual deposits has been reported[34] on the eastern side of the Cumberland Valley north and east of Waynesboro, Pa.

The Geological Survey and the Bureau of Mines, during the course of the annual barite-production canvasses since the latter part of the last century, have received reports that barite deposits also occur in Arizona (near Tombstone, Mesa, Buckeye, Salome, Parker, and Bouse), Colorado (near Canon City and Florence), Idaho (near Hailey and Troy), New Mexico (near Las Cruces and Alaman), Washington (near Springdale) and Wisconsin (near Cuba City and Mineral Point). Barite has been reported in other States, but little or no attempt has been made to exploit the deposits. Available references are given in the footnote.[35]

MINING AND PREPARATION

There is no one general method of winning barite. Mining methods are governed by the type of deposit, price of barite, cheapness of labor, availability of water, and intended use. Five methods of recovering barite have been employed in recent years and are given in their order of importance in 1944:

1. Barite-bearing clay is dug with power shovels in open pits, the clay washed out in log washers, and the log-washer concentrates further beneficiated (Missouri, Tennessee, and Georgia).

2. Barite-bearing shale is blasted in open pits and the barite separated by flotation (Arkansas).

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[33] Pit and Quarry, Vol. 23, No. 3, March 23, 1942, pp. 22-27.

[34] Stose, Geo. W., Barite in Southern Pennsylvania: Contributions to Economic Geology: Geol. Survey Bull. 225, 1903, pp. 515-516.

[35] Baker, C. L., Barite in Texas: Univ. of Texas, Bur. of Econ. Geol., Min. Resources Survey Circ. 4, Jan. 1932, 5 pp.
Grasty, J. S., The Barite Deposits of Maryland Give Promise of Becoming Important: Min. and Eng. World, vol. 41, No. 25, Dec. 19, 1914, p. 1137.
Ham, W. E., and Merritt, C. A., Barite in Oklahoma: Oklahoma Geol. Survey Circular 23, 1944, 42 pp.
Rowe, J. P., Barytes Deposits in Montana: Min. World, vol. 28, No. 16, Apr. 18, 1908, p. 637.
Talmage, S. B., and Wootton, T. P., The Non-Metallic Mineral Resources of New Mexico and Their Economic Features: New Mexico State Bureau of Mines and Mineral Resources Bull. 12, 1937, pp. 49 - 52.
Zapp, A., Barite in Northern Llano County: Univ. of Texas Bur. Econ. Geol. Min. Resc. Survey, Circ. 35, Sept. 25, 1941, 6 pp.

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3. Barite veins are mined underground, and low-grade ore is beneficiated (California, Nevada, Tennessee).

4. Massive barite is blasted in open pits with little or no subsequent sorting (Nevada).

5. Barite is mined by hand (Missouri).

Washer Operations

The prime incentive for supplanting hand mining with washer production is cost reduction. Thus, the high labor costs of World War I brought the first steam shovels and log washers to Georgia and Tennessee. Hand labor began to be displaced by the machine in Missouri during the boom years of the 1920's, but the transformation has never been so complete as in Georgia and Tennessee, and hand-mined barite competed actively with washer barite in Missouri until after the depression of the thirties. Since the beginning of World War II, a number of factors have operated to reduce hand mining in Missouri to a minimum, namely, the high wages available to unskilled labor, the general labor shortage, and the finding of the National Labor Relations Board that hand miners are the employees of the owners of the land they mine.

The typical Georgia or Tennessee producer operates somewhat as follows: Prospecting is done in areas containing fragments of barite ("float") lying on the surface or exposed in gully walls. Formerly, prospecting was limited to sinking auger holes or hand-dug test pits to depths of about 25 feet, but with the increased overburdens now encountered in the East one producer has turned to core drilling to locate and map new barite deposits.

After a deposit has been outlined, overburden, if present, is stripped by a 3/4-yard power shovel operating in conjunction with trucks (gasoline or Diesel). Some producers strip with tractors pulling 10-cubic-yard scrapers. As soon as enough overburden is stripped to permit a shovel to start mining, it moves in, and stripping and mining go on simultaneously until stripping is complete. Overburden may be up to 50 feet, and working benches are carried at about 11 feet. The shortage of shovel operators during the war has curtailed such double use of shovels. The mining shovel loads the barite-bearing clay into a truck, which carries it to the washer not over a mile away. (When this distance is exceeded, the washer is moved nearer the deposit.)

The following are the essential steps in washing barite:

The truck dumps the clay into the bullpen, a bin whose bottom is a grizzly consisting of railroad rails set about 4 inches apart. The bullpen man hydraulics the clay, rock, and barite through the grizzly with a 2-inch hose and throws aside all lumps too big to pass the grizzly. At some washers oversize rock and clay balls are thrown aside, but oversize barite is hammered through. (Rock in Georgia washers consists of jasperoid quartz and in Missouri washers of dolomite, chert, and quartz.) The slurry falls from the grizzly upon a log washer, generally with 27-foot double logs. Log overflow enters a wooden sluice leading to the mud pond. Log discharge enters a trommel, where oversize may go to a picking belt or to a jaw crusher. Undersize larger than 1 inch is crushed in rolls set at 1 inch and may be returned to the logs, trommel, or screened directly. Jigs separate the barite from rock, and ordinarily three screen sizes are produced - minus 12-mesh, plus 12-mesh minus 5/8-inch, and plus 5/8-inch. The fine-mesh material may be tabled and the iron removed with high-intensity magnetic separators to produce a high-grade (98 percent plus barium sulfate) material, or it may be added to one of the other sizes.

It is estimated that 7 to 12 percent of total barite in the clay is lost as fines in the logwasher overflow.[36] One Georgia producer has installed shaking tables and flotation cells to recover this fine material.

References on mining barite in Georgia and Tennessee not already mentioned are given in the footnote.[37]

Mining in Missouri is fundamentally the same as in Georgia and Tennessee, but certain differences make for cheaper recovery. Prospecting is easier. Washers frequently are erected in areas that hand miners have exhausted, on the theory that the hand miners left enough fine barite to support a washer. Also, overburden is rarely more than 1 or 2 feet and is often ignored by the shovel operator. Sometimes, however, it is found profitable to strip it, generally with a dragline shovel. Missouri barite tends to string out in "runs" or "leads" 10 to 20 feet wide and several hundred feet long, and the shovel operator exercises considerable insight in following the run. This practice is somewhat simpler than Georgia and Tennessee procedure, where the richer parts of the clay are very irregular vertically as well as horizontally, and mining and stripping are carried on concurrently to depths greater than 100 feet.

Missouri barite is softer than that found in Georgia and Tennessee and may be disintegrated in the trommel without the necessity of crushing. The trommel, which follows the log washer, is generally about 6 feet long by 4 feet in diameter, with holes 3/8 inch in diameter. Nearly all the barite is shattered and passes through the trommel screen, leaving lumps of unbroken quartz, limestone, and dolomite to be ejected at the discharge. The trommel concentrate contains impurities and is jigged and shipped wet or air-dried, depending on what the buyer will take.

About 1,800 gallons per minute, including 500 gallons of makeup from well, river, or spring, is needed for the average washer, producing 1,000 tons of barite a month. Local stream-pollution ordinances generally prevent turning washer waste into rivers, as it is said to kill the fish and make the water unpalatable for cattle. Therefore, a mud pond is made by throwing up an earthen dike across a little valley from which the barite has previously been mined. The dike is increased in width and height as time goes on and may reach 30 to 70 feet by the time the washer must be moved. At this stage the pond may cover 8 or 10 acres. Abandoned ponds date to the time of the first World War but, according to producers, have never completely dried up. However, crusts strong enough to support plowing teams have formed on some of the older ponds, and these have been turned to cultivation.

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[36] Hale, D. P., Jr., Modern Mining and Beneficiation of Barite at Cartersville, Ga: Am. Inst. Min. and Met. Eng. Tech. Pub. 973, 1938, p. 11.

[37] Hubbell, A. H., New Riverside - Producer of Barytes in Georgia: Eng. and Min. Jour., vol. 143, No. 10, October 1942, pp. 62-65.
--------; Barytes - a Non-metallic Product of Eastern Tennessee: Eng. and Min. Jour., vol. 144, No. 1, January 1943, pp. 63-65.
Rankin, H. S., Laurence, R. A., Davis, F. A. W., Houston, E. C., and McMurray, Lynn L., Concentration Tests on Tennessee Valley Barite: Am. Inst., Min. and Met. Eng. Tech. Pub. 880, 1938, 13 pp.
See, also, footnotes 5, 12, and 36.

A barite washer complete with double log, trommel crusher, jigs, shovel, and 4 or 5 trucks may cost $30,000 or more.

Flotation

The two largest barite producers in the United States - Magnet Cove Barium Corp. and National Lead Co. at Malvern, Ark. - recover barite from shale-replacement formation near Magnet Cove, Ark., a few miles from Malvern. The barite is "intimately mixed with quartz and small amounts of iron oxide and residual shale".[38] A typical analysis of high-grade rock shows 85.1 percent barium sulfate, 11.11 silica, and 2.85 iron oxide and alumina. Poorer samples range down to 50 percent barium sulfate. A working average seems to be about 70 percent.

The operations are open-pit, and the rock is shot down and loaded on trucks with power shovels and carried to crushers near the pit. Crushing practice differs somewhat between the two competing plants, one firm crushing a maximum-size feed for a ball mill, the other crushing somewhat finer for a jig feed before grinding. Both producers wet-grind very fine, nearly all the material passing a 325-mesh screen. The ball-mill discharge is classified and froth-floated. One firm floats barite and the other depresses it. The concentrate is filtered, dried in a rotary kiln at a temperature high enough to destroy traces of organic reagents (which would otherwise interfere with use in drilling mud), cooled, sacked in 100-pound ply bags, and shipped 400 or 500 bags to a car.

Working details of the flow sheets used by the two Arkansas producers are largely confidential; however, one satisfactory flotation method has been developed by Norman and Lindsey[39] in Bureau of Mines laboratories. Briefly, the crude material was dry-ground in a Raymond mill to 98 percent through 200 mesh, and this was fed into a ball mill with the addition of about 50 percent water and a little sodium silicate to deflocculate the pulp. The ball mill discharge was pumped to a conditioner, where coconut fatty acid was added. From the conditioner the pulp overflowed to a six-cell flotation unit and was introduced at the third cell of the unit. Flow of concentrate and tailing was countercurrent, cell to cell, giving four rougher and two cleaner cells. Pine oil was added in No. 4 cell.

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[38] Norman, James, and Lindsey, B. S. Flotation of Barite from Magnet Cove, Ark.: Am. Inst. Min. and Met. Eng. Tech. Pub. 1326, May 1941, p. 1.
[39] Work cited in footnote 38.

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Adequate dilution of the feed was obtained from froth-breaking sprays in the concentrate launders. Concentrate and tailing were collected in separate thickening cones. This process gave a 90-percent recovery of barium sulfate of the original rock, and the concentrate analyzed 98 percent barium sulfate, specific gravity 4.395 - both unnecessarily high for its use (well drilling) but indicative of the possibilities of flotation.

Underground Vein Operations

There are about three producers in this category, and their recovery methods are best discussed individually. The largest producer is the National Lead Co. at El Portal, Calif., which mines barite from a vein, the width of which "varies, showing a series of lenses, averaging 14 feet, with a maximum of 35 feet."40/ The vein has been worked on an open-cut face, but present output is obtained from subsurface operations. The "ore" is obtained by conventional drifting and shrinkage stoping, with adit levels 80 and 260 feet, respectively, below the surface. Three tons are shot in the stope and one ton is taken out immediately and the remainder later. It is crushed to pass a 4-inch grizzly at the mine and is carried via aerial tramway northward across the Merced River to the finishing plant. Here it is cone-crushed to 3/8 inch, jigged to discard about 20 percent quartz and other gangue, wet-ground in a ball mill, classified in cone classifiers, thickened in a Dorr settling tank, splashed on a steam-heated drum, scraped off with brushes, machine-sacked in 100-pound ply paper bags, and loaded on railway cars. Details are given by Young.41/

Industrial Minerals & Chemical Co. recovers barite on a small scale from the Lucky Paint mine, 26 miles northwest from Carlin, in Eureka County, Nev., by means of a shaft and stopes. The vein is 6 feet wide in places.

(See also the available information regarding the underground vein operation of Clinchfield Sand & Feldspar Co. in Tennessee, p. 8.)

Massive Barite with Open-Pit Methods

Two producers in Nevada and one in California use this procedure. The Nevada operations are quite simple. There the cut may be a pit on a hilltop or a bench on a hillside. Overburden is only about 1 foot thick and is easily stripped by power shovel. The barite is blasted down and is loaded into trucks with the shovel. In one deposit lumps of waste, mostly siliceous shale, are few and may be thrown aside by hand. In the other deposit impurities are more abundant and are removed largely by putting everything through a jaw crusher and discarding material that passes a 1-inch shaking screen. The product of both deposits analyzes 91 to 93 percent barium sulfate. Trucks carry the mineral to the Argenta siding of the Southern Pacific Railroad, where it is weighed and loaded in gondolas.

40/ Bradley, W. W., Barite in California: Rept. 25 of the State Geologist, vol. 26, No. 1, January 1930, p. 51.

41/ Young, G. J., Mining and Milling Barite: Eng. and Min. Jour., vol. 130, No. 2, July 24, 1930, pp. 70-71.

A massive California deposit is worked at the Spanish mine, 2 miles north of the town of Washington. The following information has been submitted by L. R. Moretti of the Industrial Minerals & Chemical Co. in a letter dated January 3, 1945:

> The mine is a low-grade gold-silver, lead and zinc producer and occurs in the southward extension of the famous Allegheny high-grade gold mineralization. It has been worked to a depth of 1,500 feet from the outcrop, the lower portions showing metal values in low-grade sulfides with very minor amounts of barytes. The upper portions of the mine contained oxidized ores at times very high in gold values. At an elevation of approximately 4,600 feet a barite lens on the footwall of the quartz vein was recognized, and as the mining of the gold ore at this point progressed the extent and attitude of this lens was roughly determined. In 1940, as the gold operations were being suspended, the Industrial Minerals & Chemical Co. took over the development and exploitation of this lens. Careful consideration of the slippery talcose footwall and the broken hanging wall led to the determination to extract this barite as an open-pit operation. The lens in question is approximately 400 feet long, 4 to 20 feet wide, and extends 250 feet on a 23-degree dip. Stripping operations up to December 1944 have uncovered in excess of 40,000 tons, of which some 30,000 tons have been mined. Stripping is accomplished with bulldozer, ripper, and carryall. The lens is known to continue in the same strength, purity, and dip to the 250-foot level, which would furnish in excess of 100,000 tons in reserve and to be stripped. Below the 250-foot level the vein structure plunges to a dip of 65 to 70 degrees and the barite content is reduced to 65 percent or less in much reduced width. The present production is handled by normal quarrying methods. Hand sorting provides two classes of product. The high-grade portion averages 99 percent barium sulfate and less than 0.15 iron oxide and amounts to 20 percent of total production. The rejects from this sorting average 96.5 barium sulfate with less than 1.5 percent iron oxide. Iron is present as sulfides in the ore and iron oxide fissure filling. The ore is trammed over a 7,500-foot aerial tram equipped with 20 buckets, semi-automatic loading, and automatic dumping. At elevation 3,000 the tram terminal ore bins serve as surge bins for dump-truck loading. Trucks haul to rail at Auburn, Calif., some 10 miles over dirt roads with maximum 10-percent grade and thence 40 miles over a concrete highway. Raymond roller mills at Berkeley, Calif., grind the low-grade barytes (96 percent barium sulfate) for use in oil wells and other industries where relatively high iron content is not objectionable. The 99 percent purity ore is washed in a countercurrent blind trommel and then dried and ground in roller mills for use in glass, paint, rubber, and other color-conscious industries.

Hand Mining

Until the first World War, in Georgia, and the early 1920's, in Missouri, hand mining was the sole method of recovering barite from residual deposits. Consumers preferred hand-mined barite for making bleached filler and for chemicals on account of its purity, which was generally better than 96 percent. Hand mining remained of considerable importance in Missouri until about 1939, when a decision of the National Labor Relations Board[42] to the effect that hand miners were employees of the landowners was affirmed in the Federal courts. The sudden decline of hand mining cannot be attributed solely to this decision, however, as high wages in nearby war industries undoubtedly attracted away much of the labor which might have been available for hand mining barite. Previous to the Labor Board decision the miners were considered independent contractors by the landowners. They were permitted to live in cabins on the land and paid the owner a royalty on barite mined and sold, generally 50 cents a ton. Most landowners are now reluctant to let miners dig on their property, as they believe that the miners, as employees, would have to be paid the minimum wages established by law. The average output of barite per hand miner per week is only about 2 tons (with some of his family helping), and this would be worth only $17 to the landowner, whereas wages of 40 cents an hour for a 50-hour week would be $20. The differential was even greater at the time of the Board decision.

Virtually all fields worked by hand-mining methods were first discovered when float was turned up in plowing. Next, the miners sank test pits or drove thick, pointed, steel rods into the ground at various places. If the rod touched barite, it adhered to the rod as a white powder when the rod was withdrawn. Neither dolomite nor quartz adhered. Once the "field" was established, the hand miner's prospecting method for his succeeding shafts was an insouciant combination of intuition and chance. According to testimony given before the Labor Board, the miner stood near the pit he had just depleted, threw his pick over his shoulder, and dug the next shaft where the pick fell.

The miner works the pit alone until it becomes too deep to throw out dirt with the shovel, when a crude windlass with bucket is placed over the hole, and one or two helpers assist, cleaning and sorting what the digger sends up. The shaft may be 3½ feet to 5 feet in diameter and is generally circular. The miner works down 8 to 12 feet in the shallower shafts or down to 25 or 30 feet in the deep ones, and then drifts out as much as 8 feet in all directions, until the interior of the working resembles an inverted mushroom. No timbering is used. The miner frequently is able to connect a drift of his present working with a drift of an old working, and this assists ventilation. On summer days, when air in the pit is colder than that outside, ventilation may be encouraged in a connected drift system by burning wood at the bottom of the abandoned shaft. The hot air rises, pulls in more air through the connected drifts, and fresh air falls into the new shaft. The helpers on the surface cobb off most of the adhering clay with hand mattocks, and most of the rest dries and falls off in a few days. Remaining clay and much of the iron-oxide stain is removed by vigorous treatment in the "rocker" or "rattle box" - a box on rockers, with spikes pointing inward, and with numerous holes in the bottom to permit particles of clay and iron oxide to pass. The barite is loaded on trucks and carried to the railroad or direct to the consumer.

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[42] National Labor Relations Board, Decisions and Orders: Vol. 37, Nov. 28- Dec. 31, 1941, pp. 662-672. (The Board decision was affirmed at Federal Reports 2d ser. vol. 131, pp. 585-593, and the Supreme Court denied certiorari at Supreme Court Reporter vol. 63, p. 995.)

The social side of hand mining has been noted in several articles.[43]

MANUFACTURE OF GROUND BARITE

There are two general systems of grinding barite, depending on whether it is to be bleached. Barite intended for use in well drilling is generally ground in ball mills, for contamination from the iron balls is immaterial. The same applies to filler uses in which the color does not matter. Whether the mineral is wet- or dry-ground depends on several factors. Arkansas barite must be ground before flotation and hence is wet-ground. Barite at El Portal, Calif., used for making mud-weighting material, is jigged in the same plant where ground and therefore it is simpler to grind it wet. In Georgia, after preliminary treatment in a gyratory crusher the product is ground dry in a 5-roll Raymond mill. In Missouri, unbleached barite is ground dry, and barite to be bleached is wet-ground. Nearly all ground barite is bagged automatically in multi-ply kraft bags. Manufacturers of bleached barite use a 50-pound bag, and all other grinders use a 100-pound bag.

In preparing bleached barite, considerable care must be exercised to avoid contamination from iron. The process consists of wet-grinding 5/8-inch jigged barite in a tube mill with flint pebbles, followed by thickening in a Dorr classifier; then it is bleached, vacuum-filtered, dried in a continuous kiln, dispersed in a small mill, and bagged. For this process Missouri barite has an advantage over barite found elsewhere, in that it is softer and more easily bleached.

The bleach process is generally a trade secret, but the general principles are well-known. The main impurities are the oxide, sulfide, and silicates of iron and manganese and lead sulfide. These are brought into solution by digesting the ground pulp in a hot solution of strong sulfuric acid. The pulp is settled, separated, and washed. Washing removes almost all the impurities, but traces of ferrous sulfate, which is only slightly soluble, remain and tend to oxidize to brown basic ferric sulfate or brown ferric oxide. Washing would be more effective insofar as removal of iron is concerned if the ferric sulfate could be converted to the much more soluble ferrous sulfate. This may be done by reacting the pulp from the sulfuric acid vats with a little sulfurous acid, thereby reducing ferric ions to ferrous ions.44/

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[43] Hopson, R. F., Barite Mining in Southern Missouri: Explosives Eng., vol. 14, No. 4, April 1936, pp. 107, 113.
Lieberman, H. R., Les Miserables in Missouri: Ken, Mar. 9, 1939, pp. 26-27, 47-49.
Wittich, L. L., Barytes in Missouri: The Colliery Engineer (formerly Mines and Minerals), vol. 33, No. 2, September 1912, pp. 95-97.

Most ground barite, whether bleached or unbleached, is classified so that 95 percent passes a 325-mesh screen. A small fraction of the output is ground to only 200-mesh for less-exacting filler uses.

USES OF BARITE

The chief use of barite in 1944 was in oil-well drilling; lithopone was the second largest market, chemicals third, fillers fourth, and glass fifth.

Drilling Mud

In drilling oil wells with the rotary system, a drilling bit is used which generally consists of four cutting gears rotated by a central shaft. The bit cuts or abrades the formation, and the cuttings are removed by a fluid that is forced down through the drilling shaft, out at the bit, and up the well to the surface. This fluid serves several other purposes, too, such as lubricating and cooling the bit, "plastering" the walls to prevent caving, and restraining abnormal gas and oil pressures to their formation levels. It is the last-named function in which barite is useful.

Oil fields on the Gulf Coast of Texas and Louisiana, in the San Joaquin Valley of California, and near Ventura, Calif., are noted for abnormally high gas and oil pressures; that is, oil or gas seeks to enter the well at pressures greater than that of a column of water in the well. If the oil or gas is not confined to its formation, it will blow out the well, with resulting danger to life and property. One of the early solutions to the problem of abnormal pressures was to increase the specific gravity ("weight") of the drilling fluid by adding clay to water with a little bentonite as a suspending agent. Clay drilling muds, however, are comparatively light, unless large quantities of clay are added, in which event the mud becomes too viscous. A mud is said to be too viscous when cuttings do not settle out readily in the mud ditch or if entrapped gas is unable to free itself when the fluid enters the ditch. A heavy but viscous mud may be made so light by gas "cutting" that a blowout may occur. To obtain a heavier mud without increasing viscosity, several ground materials heavier than clay have been tried, principally barite, celestite, and iron oxide.

There seems to be no logical objection to iron oxide as a weighting agent, for it is heavier than barite and, when properly prepared from native oxide, contains no detrimental soluble salts. However, it stains

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44/ De Lore, C. P., and McHan, B. B., Process of Treating Barytes: U. S. Patent 1,783,778, Dec. 2, 1930.

clothing almost indelibly, and this may be a psychological deterrent to its wider use. Since about 1938, a few thousand tons of celestite has been mined annually in Texas for use in well drilling, but celestite has the disadvantage of being lighter than barite.

Barite, because of its high specific gravity, low cost, cleanness, freedom from detrimental impurities, and inertness, is used almost universally when a heavy weighting agent is needed in drilling muds. Its use in well drilling was patented by Stroud, who assigned the patents to the National Lead Co.[45] Drillers were charged a royalty of $13 a ton until the patent expired.

Useful barite drilling muds may be obtained in specific gravities ranging up to 2.5. The barite is kept in suspension with a little bentonite.[46]

About 5 tons of barite is consumed for each 1,000 feet of high-pressure well drilled.

Glass

Barite crushed to about 16-mesh and added to the glass melt as such serves several purposes. It fluxes the heat-insulating froth that tends to form on the surface of the melt, thus saving fuel. It acts as an oxidizer and a decolorizer, makes the glass more workable, and increases brilliance in the finished ware. Fisher[47] recommended the following formulas. Window glass: Sand 100, soda ash 26, barite 4, limestone 28, and arsenious oxide 1/16 pounds. Advantages have been claimed for adding barium sulfide[48] and barium oxide[49] along with crushed barite.

Flint[50] recommends that the barite be prefused with NaCl and the melt broken up to 50-mesh by blowing a blast of air across the pouring stream. Barite enters into the melt by decomposition to barium oxide and sulfur trioxide. The sulfur trioxide combines with charcoal added to the batch specifically for this purpose, to give sulfur dioxide and carbon monoxide, both of which escape as gases. The barium oxide remaining combines with silica in various proportions. Flint suggests that the barite be reduced with zinc dust instead of carbon.[51] In such case the formula is: Sand 1,000, soda ash 350, limestone 200, barite 50, arsenic 5, and zinc 5 pounds.

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[45] Stroud, B. K., Application of Mud-laden Fluids to Oil or Gas Wells: U. S. Patents 1,575,944 and 1,575,945, March 9, 1926.

[46] Stern, A. Geo., Role of Clay and Other Minerals in Oil-Well Drilling Fluids: Bureau of Mines Rept. of Investigations 3556, February 1941, pp. 53-54.

[47] Fisher, E. E., Glass and Its Manufacture: U. S. Patent 1,665,693, 1928.

[48] Fisher, E. E., Glass and Its Manufacture: U. S. Patent 1,665,694, April 10, 1928. Also, Glass and Process of Making Same: U. S. Patent 1,962,495, June 12, 1934.

[49] ______, Glass Composition: U. S. Patent 1,962,496, June 12 1934.

[50] Flint, F. C., Use of Barium Sulfate in Glass Batches: U. S. Patent 1,986,720, Jan. 1, 1935.

[51] Flint, F. C., Glass Batch: U. S. Patent 2,113,195, April 5, 1938.

Nearly all large glass furnaces operated on a continuous basis, for example, those making window glass and container glass, use crushed barite as a surface flux, replacing in a large degree crushed salt cake formerly used for this purpose. Barite is added, preferably as crushed material of about 16 to 20 mesh, because this screen size is fine enough to go into solution rapidly and yet not so fine that it coalesces in small lumps, which dissolve more slowly and may form seeds. However, when crushed material is not available, the glass industry uses ground barite originally intended for use in well drilling.

As fluorine is a constituent of many glasses, barite containing fluorine may find a market in the glass industry, although it would be worthless in making chemicals or lithopone. A mixed barite-fluorspar mined near Marion, Ky., known as fluorbarite, containing typically 70 percent fluorspar and 30 percent barite, may be crushed to 20 to 40 mesh and used with sand, soda, lime, and feldspar in making clear glass.52/ Magnesium chloride is added to the melt to volatilize iron impurities as ferric chloride.

Filler

The index of refraction of barite is low (1.6 plus); consequently the ground mineral has little hiding power in a drying oil vehicle, and its use in paint is limited to that of filler or extender. In this role it offers low oil absorption and fair sanding properties and contributes to a dense, nonporous film. Considerable quantities of barite can be incorporated without bodying, owing to the low oil adsorption. Its low tinting strength makes ground barite a good base for both colored and white pigments. Disadvantages claimed are its relatively high cost, its failure to protect exterior paint films from ultraviolet light, and its tendency to cause settling and caking in the paint can. That its advantages far outweigh its defects is evidenced by sales of ground barite to the paint industry, which were estimated by the Bureau of Mines and the producers at 23,000 short tons in 1944.

Ground barite is also used as a filler in inks, oilcloth, linoleum, rubber, X-ray-proof fabricated walls, asbestos brake linings, and other materials. Ground barite is said to decrease the time required for rubber-sulfur mixtures to reach their maximum tensile strength, but acts merely as a diluent, causing a progressively decreasing quality with increase in the volume added. (Blanc fixe on the other hand improves the quality increasingly up to a certain limit.)53/

Lithopone

Lithopone is an extremely intimate mixture of two coprecipitated salts - zinc sulfide and barium sulfate. Theoretically, it contains 29.4

52/ Harth, P. E., Manufacture of Glass: U. S. Patent 2,218,334, Oct. 15, 1940.

53/ Dawson, T. R., Barytes and Its Employment in the Rubber Industry: India Rubber Jour., vol. 73, 1927, pp. 885-889, 926-930, 961-966.

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percent zinc sulfide and 70.6 percent barium sulfate. Actually, it contains small quantities of other compounds, some of which are added intentionally to increase its stability. The coprecipitation of zinc sulfide and barium sulfate has been known for 200 years or more, but the precipitation product had little value as a pigment owing to its low hiding power and its tendency to darken. An Englishman, J. B. Orr, solved both problems by heating the air-dried precipitate in an externally fired furnace to a red heat, causing a change in the crystalline structure of the salts, which resulted in a higher refractive index. "Orr's white", introduced in 1874, was the forerunner of modern lithopones.

Barite enters the manufacture of lithopone in the following way: Crude barite is crushed at the lithopone plant in a cone crusher to about 5/8-inch, then in a hammer mill or in rolls to a range of 10 to 100 mesh. However, if the material is crushed too fine, dust losses will be high in the rotary kiln. The crushed barite is mixed with some form of carbon, generally coal of the same mesh size, but petroleum coke breeze also may be used. The mix is introduced at one end of the furnace, which may be fired with oil or powdered coal, and black ash (black granules that resemble cinders) appear at the discharge end. The hot zone of the kiln may range in temperature from 2,100° to 2,400° F. According to one theory, the following reaction takes place: $BaSO_4$ (100 pounds) + 4C (21 pounds) → BaS (73 pounds) + 4CO (48 pounds). Hirschel[54] notes, however, that since an equally good yield of BaS is obtained if only 17 pounds of C is used to 100 pounds of $BaSO_4$, the reaction probably proceeds as follows: $BaSO_4 + 2C \rightarrow 2CO_2 + BaS$. Any C remaining then reacts with the CO_2 present, so that the discharge gases are a mixture of CO and CO_2. In general practice, however, 20 parts of coal are used to 100 parts of barite.

In addition to carbon, black ash contains other impurities, consisting of unreduced $BaSO_4$ and the nonvolatile constituents of both coal and crude barite. BaS comprises only 75 to 85 percent of the total. The hot black ash is quenched in hot-water tanks and digested until its barium sulfide content has been extracted.

Barium monosulfide itself is only slightly soluble in water, and the question naturally arises, how can black ash be leached to give a solution of barium sulfide. The answer is, barium sulfide hydrolyzes readily according to the (idealized) equation: $2\,BaS + 2H_2O \rightleftharpoons Ba(OH)_2 + Ba(SH)_2$. However, as all products are assumed ionized, the equation is best represented thus: $Ba^{++} + S^{--} + H_2O \rightleftharpoons Ba^{++} + OH^- + SH^-$. Simplifying: $S^{--} + H_2O \rightleftharpoons OH^- + SH^-$. The extent of hydrolysis is determined from the formula:

$\frac{h^2}{v(1-h)} = K_{H_2O}/K\,acid$, where h = fraction of BaS hydrolyzed, K_{H_2O} = ionization constant of water, K_{acid} = ionization constant of $HS^- \rightleftharpoons S^{--} + H^+$, and v = number of liters of solution containing one mole of BaS. (A typical solution of BaS is 1.2 molar, so that v = 0.83 liter.) Substituting values in the formula, using constants for a reaction at 70° C:

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[54] Hirschel, W., Die Fabrikation von Schwefelbarium: Chemiker-Zeitung, vol. 50, No. 88, Sept. 15, 1926, pp. 692-3.

$\frac{h^2}{0.83\ (1-h)} = \frac{15 \times 10^{-14}}{1.2 \times 10^{-15}}$, thus h = 0.99 or 99 percent. It will be seen that hydrolysis of BaS approaches 100 percent as temperature is increased and concentration is decreased. It is important that hydrolysis does not proceed according to the equation: $BaS + H_2O \rightarrow Ba(OH)_2 + H_2S$, which would lose H_2S as a gas and prevent precipitation of zinc as the sulfide. That hydrolysis does not proceed to that extent may readily be appreciated from the following considerations: Hydrogen sulfide will be evolved when the product of the concentrations of HS^- and H^+ in the solution exceeds the ionization constant of the acid, and then only if the molecular H_2S so formed more than saturates the solution. In the equation $\frac{(H^+)\ (HS^-)}{(H_2S)} = K_{ion}$, K_{ion} is known to be 9×10^{-8}; (H^+) is determined to be 12.5×10^{-14} from a consideration of the concentration of OH^- in the hydrolyzed solution; $(HS^-) = 0.99 \times 1.2$ or about 1.2; substituting in the equation and solving, $H_2S = 1.7 \times 10^{-6}$. The solubility of H_2S as determined from the solubility tables is 3.2×10^{-2} moles per liter. A solution of 1.2 molar BaS at 70° C. is therefore only 0.5 percent saturated with respect to H_2S, owing to the repression of H+ by the OH^- formed in hydrolysis. Even at 90° C., H_2S is only a little less than half as soluble as at 70° C. Near-boiling temperatures are necessary to drive off all H_2S.

The addition of a zinc sulfate solution to the black ash leach liquor has the effect of reversing hydrolysis and tying up virtually all S^{--} as insoluble ZnS, and the pH drops correspondingly toward neutrality. As the stability of lithopone to light is enhanced by a slight alkalinity in the finished product, the barium sulfide liquor is generally in excess in the precipitation reaction. The precipitate is collected, washed, dried, calcined, quenched in water, wet-ground, dried once more, and bagged. A sample range of analyses is:[55]

	Percent
Moisture	0.06 to 0.35
Soluble salts and impurities	.08 to 1.50
ZnO	.03 to 2.96
ZnS	23.10 to 29.36
$BaSO_4$	67.43 to 75.41

The first lithopone plant in the United States was built by the Beckton Chemical Co. at 272 Passaic St., Newark, N. J., in 1892, and 4 years later a second plant was built on the land of Harrison Bros. & Co., Philadelphia. Krebs Pigment & Chemical Co. next erected a lithopone plant at Newport, Del., and at about the same time the Grasselli Chemical Co. and the N. Z. Graves Co. also entered the field.[56] The Cawley-Clark Co. built a plant in Newark, N. J., in 1903.[57]

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[55] Eeaton, N., Outlines of Paint Technology: 2d ed., 1940, p. 90.

[56] Tyler, P. M., Trends in White Pigment Consumption: Bureau of Mines Inf. Circ. 6881, 1936, p. 7.

[57] Peters, E. V., Zinc Oxide and Lithopone: Chem. Age., vol. 31, No. 5 May 1923, p. 234.

Lithopone production data were first compiled in 1906 by the Geological Survey, and in that year output was recorded at 5,149 tons. Production has since expanded tremendously. (See table on p. 70.) Ever since the middle twenties, however, an early demise for lithopone has been predicted on account of the greater capacity of the titanium oxide pigments recently developed. Titanium dioxide has the greatest hiding power of all the white pigments, as shown in the following table:[58]

Pigment	Hiding power (white lead = 100)
Zinc sulfide	367
Lithopone	160
Antimony oxide	180
Titanium dioxide	480
Zinc oxide	147

Thus, when 1 pound of TiO_2 will do the work of 3 pounds of lithopone or 4.8 pounds of white lead, it may well be wondered why other white pigments are able to stay on the market. They do so chiefly because of the greater cost of titanium pigments. In November 1944, titanium dioxide was selling at 15 cents a pound bulk, whereas lithopone sold at 4¼ cents. The future of lithopone depends just as much on the price of barite as on competition from titanium dioxide. Though lithopone is only 70 percent $BaSO_4$, 1 ton of crude barite is consumed for each ton of lithopone produced. Crude barite delivered at the lithopone plant for $10 to $14 a short ton accounts for a substantial fraction of the cost of finished lithopone, and barite producers selling to lithopone makers must therefore keep their costs down if they are to preserve this market.

Manufacture of Barium Chemicals

General. - Barite is extremely insoluble, and to make it available for chemical purposes it must be converted to a water-soluble material. If it is to be made into blanc fixe, however, it may be dissolved in sulfuric acid and precipitated therefrom, as described on page 30, without passing through a water-soluble stage. But for other barium products a process must be chosen that will yield a soluble intermediate material. Although barium sulfate is 17 times less soluble than barium carbonate at 100° C., barite may be converted to the carbonate, an ideal starting material for other barium chemicals, by digestion with a sodium carbonate solution under pressure at elevated temperature. Ipatieff and Freitag[59] note that the aqueous reaction $BaSO_4 + 2Na_2CO_3 \rightarrow BaCO_3 + Na_2CO_3 + Na_2SO_4$ is 97 percent complete after digesting 4 hours at 320° C. under 100 atmospheres pressure. So far as is known, the process has never been tried commercially.

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[58] Mills, H., Characteristics of Lithopone and Zinc Sulfide Pigments for Paint Manufacture: Chem. Ind., vol. 38, No. 5, May 1936, p. 481.

[59] Ipatieff, V. N., and Freitag, C., Double Decomposition and Oxidation of Inorganic Compounds under Pressure: Ind. and Eng. Chem., ind. ed., vol. 27, No. 3, March 1935, pp. 342-343.

It may be of interest to note the more important processes for getting barite into solution which have enjoyed commercial success in the past, together with some that have been proposed but never adopted commercially.

Melts and associated methods. - There have been a number of proposals to obtain a soluble barium compound by double decomposition in a melt. Some of the procedures are listed. Gardner[60] fused barite with calcium chloride for 15 minutes at 1,100° C. Some SO_3 was evolved. The mix was cooled, crushed, and leached with water to yield 70 percent of the theoretical $BaCl_2$. Shreve, et al,[61] found that lower temperatures (100° to 200° C.) could be utilized if one part of ground barite and two parts calcium chloride were digested in one and one-half parts water for 3 to 12 hours and the cooled mass leached with a mixture of three parts methanol and one part ethylene glycol. Barium and calcium chlorides are soluble in this medium and may be recovered from the solvent by evaporation. The mixed salts are then differentially crystallized from water. A variant of this method has been introduced by Hill and Isenberg.[62] Ground barite is dissolved in molten caustic soda. The mass is cooled, crushed, and leached with a solution consisting of three parts ethylene glycol and one part methanol. The solvent dissolves $Ba(OH)_2$, which may be recovered by distilling off the solvent.

Silica processes. - Some furnacing methods attempt to bypass the formation of black ash and to arrive at a soluble barium product in some other way. Such methods are not used commercially in the United States but have considerable theoretical interest.

One such method is the reaction of barite with silica to form a water-soluble barium silicate, which hydrolyzes to yield barium hydroxide. Patents on this method are given in a footnote.[63] This process is not to be confused with the Deguide process for converting witherite (natural barium carbonate) to barium silicate (see p. 56). Fisher[64] substitutes bauxite for part of the silica, and De Jahn[65] suggests calcium or magnesium silicate as a source of silica.

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[60] Gardner, H. A., Process of Making Barium Chloride: U. S. Patent 1,146,491, July 13, 1915.

[61] Shreve, R. N., Pritchard, W. N., Farr, W. V., Still, A. J., and Crosby, J. D., Process of Manufacturing Soluble Salts of Barium and Strontium: U. S. Patent 2,030,659, Feb. 11, 1936.

[62] Hill, L. O., and Isenberg, S., Method for Producing Compounds of Barium and Strontium: U. S. Patent 2,225,633, Dec. 24, 1940.

[63] Meade, G. P., and Traxler, R. N., Method of Producing Soluble Barytic Material for Use as a Sugar Precipitant: U. S. Patent 1,884,796, Oct. 25, 1932.
Rothe, F., and Brenek, H., Process for Transforming the Barium and Strontium Sulfates: U. S. Patent 1,772,269, Aug. 5, 1930.
Ruesberg, F., and Clauss, G., Manufacture of Barium Hydroxide: U. S. Patent 1,799,989, April 7, 1931.

[64] Fisher, E. E., Manufacture of Barium Compounds: U. S. Patent 2,105,940, Jan. 18, 1938.

[65] De Jahn, F. W., Process of Decomposing Barium Sulfate: U. S. Patent 2,232,100, Feb. 18, 1941.

Reduction and decomposition reactions. - The batch furnace process was the earliest commercial process for getting barite into solution. Even in the 1890's it was still very inefficient, and the black ash of this period contained about 40 percent unconverted barite.[66]

Crushed coal and petroleum coke breeze are the classical reducing agents in making black ash, but presumably reduction could be accomplished by a reducing atmosphere alone. Ekstrom[67] proposed that hydrocarbons derived from oil be the sole reducing agent in conjunction with a muffle furnace. After passing over the barite in the furnace, the incompletely oxidized gases were burned as fuel for the flames around the furnace.

Jacobs proposed heating barite in an electric furnace, driving off most of the sulfur, forming a mixture consisting mostly of oxide. The mixture was digested in water and barium hydroxide crystallized out.[68] Newberry and Barrett[69] patented a similar process for driving off sulfur, using a rotary kiln at 2,700° F. The barite was prevented from fusing into a mobile mass by the addition of MgO, which assisted in pelletizing the material as it moved down the kiln.

Fulton[70] proposed an electric resistance furnace to make black ash.

None of these processes appears to have attained commercial success, and the standard procedures for obtaining soluble barytic materials from barite are all based on black ash as a starting point.

Blanc fixe. - Blanc fixe, artifically precipitated barium sulfate, is made by mixing together solutions of a soluble barium salt (such as the sulfide) and sodium sulfate, whereby blanc fixe is immediately precipitated. Also, a substantial quantity of byproduct blanc fixe is obtained in the manufacture of hydrogen peroxide by the barium peroxide process: $BaO_2 + H_2SO_4$ (dilute solution) → $H_2O_2 + BaSO_4$ (blanc fixe). This blanc fixe is generally slightly lower in grade than that made by the first-mentioned process. In one commercial process, hydrogen peroxide is produced by reacting phosphoric acid with barium peroxide; then the resulting barium phosphate is treated with sulfuric acid to yield blanc fixe and more phosphoric acid.

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[66] Jacobs, C. B., Process for Manufacturing Soluble Barium Compounds; U.S. Patent 624,041, May 2, 1899.

[67] Ekstrom, A. W., Process of Manufacturing Barium and Strontium Compounds: U. S. Patent 1,067,595, July 15, 1913.

[68] Jacobs, C. B., Process for Manufacturing Soluble Barium Compounds: U. S. Patent 624,041, May 2, 1899; and Process of Preparing Barium Hydrate:. U. S. Patent 720,927, Feb. 17, 1903.

[69] Newberry, S. B., and Barrett, H. N., Process of Making Barium Hydrate: U. S. Patent 1,106,578, Aug. 11, 1914; same authors, Process of Producing Barium Oxide: U. S. Patent 1,133,392, Mar. 30, 1915.

[70] Fulton, C. H., Process of Electrical Reduction: U. S. Patent 1,267,347, May 21, 1918.

It was early noted that considerable expense would be saved if blanc fixe could be produced directly from crude barite without passing through the black-ash stage. As barium sulfate is soluble in concentrated sulfuric acid (presumable forming $Ba(HSO_4)_2$) and almost insoluble in dilute sulfuric acid, it has been suggested that barite be dissolved in concentrated sulfuric acid and the solution diluted with water.[71] Refinements of this method[72] include the use of oleum (fuming sulfuric acid) and the addition of excess ground barite, so that barium sulfate precipitates first as a complex with sulfuric acid, such as $BaSO_4.H_2SO_4$. This slurry is diluted, and blanc fixe is precipitated. The sulfuric acid process has not been practiced commercially.

A theoretical alternative is to dissolve barite in a melt of soluble salts, then lixiviate the mass with water. A pulp of blanc fixe is left behind. Moffatt[73] used sodium sulfate as the solvent. Moore[74] suggested that the fusion mass be a mixture of sodium chloride and alkali metal nitrates and carbonates. The nitrates and carbonates were intended to render soluble the impurities in the crude barite, such as iron and lead sulfides and iron silicates. Or the insoluble impurities may simply be allowed to settle, according to Lichtenberger.[75] McCallum[76] proposed a continuous fusion process, ground barite and salt being fused in a rotary kiln, the melt dropping into water. If the crude barite is contaminated with gypsum, barium carbonate may be added to the melt to remove calcium as the carbonate.[77] These melt processes have not been adopted commercially so far as is known.

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[71] Walker, J. P., Process of Making Precipitated Barium Sulfate: U. S. Patent 1,040,594, Oct. 8, 1912.

[72] D'Adrian, A.L.D., Process for the Production of Barium Sulfate: U. S. Patent 1,981,094, Nov. 20, 1924.
Roberts, E. J., et al., Manufacture of Finely Divided Precipitates: U. S. Patent 2,161,651, June 6, 1939.
Roberts, E. J., Manufacture of Barium Sulfate: U. S. Patent 2,161,652, June 6, 1939.
Work, L. T., et al., Manufacture of Barium Sulfate; U. S. Patent 2,161,650, June 6, 1939.

[73] Moffatt, A., Pigment: U. S. Patent 973,373, Oct. 8, 1910.

[74] Moore, G., Process of Manufacture of Blanc Fixe: U. S. Patent 1,388,285, Aug. 23, 1921.

[75] Lichtenberger, T., and Kaiser, L., Process for Manufacturing Pure, White, and Finely Distributed Sulfate of Barium and Sulfate of Calcium: U. S. Patent 1,822,815, Sept. 8, 1931.

[76] McCallum, J., Method of Making Sulfates of Barium and Calcium: U. S. Patent 2,039,432, May 5, 1936.

[77] Englert, C., et al., Process for Making Blanc Fixe of Particular Softness: U. S. Patent 2,033,696, Mar. 10, 1936.

Another theoretical alternative is to bake a slurry of ground barite in a solution of calcium chloride and then disintegrate the dry cake of complex salt in water, whereby blanc fixe is precipitated.[78]

As mentioned before, the standard method of making blanc fixe is to add a solution of sodium sulfate to a solution of barium sulfide. This procedure gives a product of sufficient purity and fineness of grain for most purposes. According to Pierce,[79] the reaction preferably proceeds as follows:

> A solution of barium sulfide is caused to interact with a solution of sodium sulfate, the barium sulfide being maintained in excess, throughout the precipitation, of that theoretically required to satisfy the sodium sulfate. The temperatures of the solution of barium sulfide and sodium sulfate are maintained at such points that the temperature of the mixture in the precipitating vessel will range between 50° C. and 100° C., preferably from 60° to 75°, throughout the precipitation. Between these temperatures the precipitated barium sulfate is finer than if the solution were colder, and furthermore the precipitated barium sulfate * * * tends to settle much faster in the precipitating vessel, with a consequence that the top liquor and subsequent wash solution can be decanted off in a more satisfactory manner. It is important that the strength of the barium sulfide solution should be between the ranges of 12 percent and 20 percent of barium sulfide content and also that the strength of the sodium sulfate solution should be between the ranges of 20 to 30 percent sodium sulfate content.

The precipitate is washed in iron-free water maintained at a temperature between 60° and 75° C. The material so produced is slightly alkaline, but the alkalinity is not a deterrent for most of the uses of blanc fixe. However, if it is used in printing inks, it attacks the copper plates of the printing surfaces, and its alkalinity also renders it unsatisfactory as a rubber filler. Pierce later suggested that neutral blanc fixe could be made by washing the precipitate with a weak solution of oxalic acid and calcining the product to burn off the acid.[80] The same inventor also proposed the niter-cake-barium carbonate process for obtaining neutral blanc fixe. Here a barium carbonate slurry may be treated with a solution of niter cake (crude $NaHSO_4$ containing a little free H_2SO_4), the niter cake being slightly in excess of the barium carbonate, and the following idealized reaction occurs: $2NaHSO_4 + BaCO_3 \longrightarrow BaSO_4 + Na_2SO_4 + CO_2 + H_2O$. The liquors are decanted from the precipitate, which is washed until the wash waters register alkaline to methyl-orange indicator and acid to phenolphthalein (or a pH between 4.0 and 8.3). The near-neutrality is said to be caused by a small amount of alkaline barium carbonate in the blanc fixe, which serves to neutralize adsorbed acid.[81] Whether these refinements have ever been applied commercially is not known. The problem of obtaining a neutral blanc fixe has also been met, at least theoretically, by using ammonium sulfate instead of sodium sulfate as the source of sulfate ions, when used with barium sulfide solutions. Barium sulfide hydrolyzes to give an alkaline solution, ammonium sulfate hydrolyzes to give an acid solution, and the precipitation is thus carried out in a virtually neutral solution[82]

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[78] Farr, H. V., Process for Refining and Purifying Barium Sulfate: U. S. Patent 1,752,244, Mar. 25, 1930.

[79] Pierce, J. B., Jr., Method of Making Precipitated Barium Sulfate and Sodium Sulphydrate: U. S. Patent 1,457,934, June 5, 1923; and Method of Making Barium Sulfate: U. S. Patent 1,457,935, June 5, 1923.

[80] Pierce, J. B., Jr., Manufacture of Neutral Blanc Fixe: U. S. Patent 2,320,980, June 1, 1943.

The method of making blanc fixe may depend in some degree upon the byproducts desired. For example, if sodium acid sulfide (sodium sulfhydrate), NaSH, is desired instead of sodium sulfide, the barium sulfide liquer may be reacted with CO_2, so that half the barium is precipitated as the carbonate, the other half remaining in solution according to the equation: $2BaS + CO_2 + H_2O \rightarrow BaCO_3 + Ba(SH)_2$. The barium carbonate may then be separated and a solution of sodium sulfate added to the solution of $Ba(SH)_2$ to precipitate blanc fixe, leaving NaSh as a byproduct.[83]

Special processes for obtaining blanc fixe suitable for rubber filler are given in the footnote.[84]

Some interesting variants in raw materials have been proposed.[85]

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[81] Pierce, J. B., Manufacture of Blanc Fixe: U. S. Patent 1,828,846, Oct. 27, 1931.

[82] McQuaid, H. S., Blanc Fixe: U. S. Patent 2,006,219, June 25, (1935).

[83] Pierce, J. B., Jr., Barium Sulfate and Method of Making Same: U. S. Patent 1,765,737, June 24, 1930.

[84] Peirce, G. A., Alkaline Earth Metal Sulfate: U. S. Patent 2,044,954, June 23, (1936). (Precipitation conducted in presence of dispersing agent consisting of a soap and phosphate ions.)

Pierce, J. B., Jr., Blanc Fixe and Method of Making Same: U. S. Patent 2,081,835, May 25, 1937. (Barium sulfide reacted with dilute H_2SO_4 in presence of casein, which coats particles of blanc fixe formed).

[85] Gilman, W. D., Process of Obtaining Sulfate of Barium and Chloride of Zinc: U. S. Patent 746,954, Dec. 15, 1903. (Uses barium chloride and zinc sulfate.)

Hall, D. C., et al., Process of Making Pigment Barium Sulfate from Barium Chloride: U. S. Patent 2,125,342, Aug. 2, 1938. (Uses barium chloride and sulfuric acid).

Jacobs, C. B., Process of Producing Caustic Soda and Barium Sulfate: U. S. Patent 737,740, Sept. 1, 1903. (Uses barium hydroxide and sodium sulfate.)

Mueller, M., Process of Producing Barium Sulfate from Barium Sulfide: U. S. Patent 2,094,902, Oct. 5, 1937. (Uses barium sulfide and sulfuric acid.)

Philip, J., Improvement in the Manufacture of Artificial Sulfate of Baryta: U. S. Patent 120,771, Nov. 7, 1871. (Uses barium chloride and magnesium sulfate.)

Sequine, W., Jr., Preparation of Blanc Fixe: U. S. Patent 1,863,699, June 21, 1932. (Uses barium chloride and gypsum.)

Weber, I. E., and Wood, W. S., Manufacture of Barium Sulfate: U. S. Patent 2,285,242, June 2, 1942. (Uses barium sulfide and sulfuric acid in presence of phosphoric and hydrochloric acids.)

Barium chloride. - It might be supposed that barium chloride could be recovered from black-ash leach liquors by the addition of a cheap alkali metal chloride (such as common salt) more soluble than $BaCl_2.2H_2O$ and cooling and/or evaporating the solution until substantially all the barium crystallizes as the hydrated chloride. However, in actual practice it was found that barium chloride so deposited contained a considerable amount of sulfur-bearing barium compounds, possibly $Ba(SH)_2$, BaS, or both, in addition to codeposited reactant. It was found that if the solution were saturated with H_2S, fairly pure crystals of $BaCl_2.2H_2O$ could be obtained. However, such a solution was impractical to work with on account of a continuous evolution of H_2S, and it was proposed that the solution be incompletely saturated with H_2S so that escaping H_2S would be negligible.86/

By this method, a good initial crop of $BaCl_2.2H_2O$ crystals was obtained, but on further evaporation impure crystals were again formed. In view of these difficulties, the standard method of making barium chloride in the United States for many years was to add calcium chloride to the calcining mix, so that the black ash so produced contained barium chloride instead of sulfide. This method is no longer used, as more efficient recoveries are available through improved systems. One of the modern processes is that of Mertes,87/ who proposed that, since the function of the H_2S was simply to tie up sulfide ion as HS^- without creating OH^-, one could effect the stabilization of HS^- simply by adding hydrochloric acid to the solution until pH $\doteq$ 7, or thereabouts. And the inventor found an even cheaper method of forming a $Ba(SH)_2$ solution substantially free of OH^-. By adding an amount of $CaCl_2$ equivalent to the amount of OH^- in the solution, he obtained a precipitate of $Ca(OH)_2$, which was removed, leaving a slightly alkaline solution containing Ba^{++}, HS^-, and Cl^-. Common salt is then added, and $BaCl_2.2H_2O$ crystallizes out when the solution is cooled. Recovery was 83 percent of theoretical, and the $BaCl_2.2H_2O$ so formed was 99.5 percent pure.

Another standard process in present-day use is that of Specht.88/ A 20-percent barium sulfide solution is heated to between 60° and 80° C., and hydrochloric acid is added until the solution is only slightly alkaline. Insoluble impurities are allowed to settle. (A pH of 7.7 is enough to precipitate many of the common heavy metal sulfides, thus removing Mn, Zn, Ni, Co, Sn, Pb, etc.) The supernatant liquor is separated and slightly acidified with more HCl. The solution now consists of barium chloride with impurities. Chlorine gas and air are blown into the solution to oxidize residual iron and sulfur, which impurities are permitted to settle out as the hydroxide and element, respectively. The liquor is neutralized with barium carbonate or hydroxide and filter-pressed; barium chloride crystals are salted out, filtered, and dried. Byproduct H_2S may be burned to recover S.

86/ Jahl, A., Process for the Production of Soluble Barium Salts: U. S. Patent 1,529,435, March 10, 1925.

87/ Mertes, A. T., Process of Making Barium Salts: U. S. Patent 1,936,849, Nov. 28, 1933. (Assigned to Krebs Pigment & Color Corp.)

88/ Specht, R. C., Method of Making Barium Chloride: U. S. Patent 2,204,192, June 11, 1940. (Assigned to Barium Reduction Corp.)

Two unusual methods of making barium chloride are cited in the footnote.[89] They are not used commercially.

Barium carbonate. - The most obvious method of making barium carbonate is to add soda ash to a solution of barium sulfide, and indeed this is a general commercial process. One objection, however, is that the soda ash of commerce contains impurities of heavy metals, Fe, Pb, and others, which, though present in very small quantities, may discolor the barium carbonate precipitate by forming colored, insoluble sulfides. Such barium carbonate is less suitable for use in glass and enamel manufacture than sulfide-free carbonate. Therefore, it has been suggested that the soda ash be pretreated with a sodium sulfide solution to remove insoluble sulfides before reaction with barium sulfide.[90]

Another basic process in commercial use is the reaction of barium sulfide solution with CO_2 gas, whereby $BaCO_3$ is precipitated:

$$\begin{array}{c} \mathrm{2BaS + 2H_2O \rightarrow \underline{Ba(SH)_2 + Ba(OH)_2}} \\ \downarrow + \mathrm{CO_2} \\ \mathrm{BaCO_3 + Ba(SH)_2 + H_2O} \end{array}$$

As all soluble products are assumed ionized, the equation reduces to: $2Ba^{++} + CO_3^{--} \rightarrow BaCO_3 + Ba^{++}$. As recommended by Pierce,[91] the reaction is best stopped at this point, for in completing the saturation troublesome H_2S is liberated, and various oxysulfur compounds tend to precipitate along with the $BaCO_3$. By stopping the reaction when only half the barium is precipitated as carbonate, a solution of $Ba(SH)_2$ is left, which has commercial value, for example in making blanc fixe by addition of Na_2SO_4.[92] Pierce later found that all the Ba could be recovered from solution, giving a fairly pure, dense carbonate, if an amount of sodium sulfide (available as a byproduct of blanc fixe manufacture) equivalent to one-half the barium were added to the solution.[93] The following idealized reactions are assumed:

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[89] Gilman, W. D., Process of Obtaining Sulfate of Barium and Chloride of Zinc: U. S. Patent 746,954, Dec. 15, 1903. (BaS solution + $ZnCl_2$ solution $\rightarrow$ $BaCl_2$ solution + ZnS precipitate).
Granoe, E. V., Process of Manufacturing Barium Chloride: U. S. Patent 1,167,061, Jan. 4, 1916. (BaS solution + Cl_2 gas $\rightarrow$ $BaCl_2 + S$.)

[90] Weber, I. E., and Wood, W. S., Manufacture of Barium Carbonate: U. S. Patent 2,315,472, Mar. 30, 1943.

[91] Pierce, J. B., Jr., Process of Making Precipitated Barium Carbonate and Barium Sulphydrate: U. S. Patent 1,634,338, July 5, 1927.

[92] Alvord, E. B., Process for the Production of Sodium Hydrosulfide and Valuable Byproducts: U. S. Patent 1,650,106, Nov. 22, 1927.

[93] Pierce, J. B., Barium Carbonate and Sodium Sulphydrate Manufacture: U. S. Patent 1,774,523, Sept. 2, 1930.

$$\begin{tikzcd} 2\,BaS + 2H_2O \arrow[r] & \underline{Ba(OH)_2 + Ba(SH)_2} \arrow[d, "+2Na_2S + 2CO_2"] \\ & 2BaCO_3 + 4\,NaSH \end{tikzcd}$$

The NaSH is a valuable byproduct.

As before noted, if all the barium carbonate is precipitated with CO_2 from a solution of BaS alone, the precipitate carries down with it certain sulfur impurities. Some methods proposed for removing these impurities from $BaCO_3$ are given in the footnote.[94]

A "superreactive" $BaCO_3$ of very fine particle size for use in brine purification may be made by violent agitation of the BaS solution as the CO_2 is added.[95]

The possibility of converting barium sulfate into barium carbonate has been discussed (p. 27).

Barium oxide and peroxide. - The standard method of making barium oxide (almost all of which is consumed in the producing plant in $Ba(OH)_2$ and BaO_2) is to heat pellets of $BaCO_3$ mixed with carbonaceous matter in an electric arc furnace at about 2,500° C. The carbon speeds the reaction by reducing evolved CO_2 to CO. The CO thus formed serves to dilute the CO_2 next evolved, thus reducing its partial pressure and its tendency to recombine with BaO. The decomposition then proceeds easily according to the equation:

$$\begin{tikzcd} BaCO_3 \arrow[r, "heat"] & BaO + CO_2 \arrow[d, "+C"] \\ & 2CO \end{tikzcd}$$

The core of the batch fuses and decomposes to BaO, and a shell of undecomposed $BaCO_3$ pellets suffices to contain the reaction. When the batch cools, the shell is knocked off and used in the next furnacing. The BaO is broken up with sledge hammers, put through jaw and roll crushers, and is then ready for use in making BaO_2 or $Ba(OH)_2$.

The fundamentals of making BaO do not appear to have changed in 50 years or more. In the old days much effort and thought was expended to get a porous BaO for use in making BaO_2, but the dense product obtained in the electric furnace can be oxidized easily to BaO_2, so that there is no longer any point in the elaborate precautions urged in the early stages of the art. To make BaO_2, BaO ordinarily is heated in a current of air under pressure in a rotating drum. Steel balls in the drum continually break up fresh surfaces even in dense barium oxides, so that oxidation to BaO_2 proceeds smoothly.[96]

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[94] Mardwedel, J. E., and Looser, J., Process of Purifying Barium Carbonate: U. S. Patent 1,673,985, June 19, 1928. (Moist $BaCO_3$ heated with NaOH and leached to remove impurities.) Same inventors: Process for Making Barium Carbonate, U. S. Patent 1,615,515, Jan. 25, 1927. ($BaCO_3$ precipitated with CO_2 in presence of Na_2CO_3 is freer from S than when Na_2CO_3 omitted.)
Falco, F., Process for the Manufacture of Pure Barium Carbonate: U. S. Patent 1,640,652, Aug. 30, 1927. (Moist $BaCO_3$ heated with oxalic acid.)

[95] Pierce, J. B., Jr., Method of Purifying Brines: U. S. Patent 2,191,411, Feb. 20, 1940.

The old Brin process of making BaO_2 as a source of oxygen and H_2O_2 is of historical interest only.[97]

Some other proposed processes are given in the footnote.[98]

Barium hydroxide. - Two standard methods of making barium hydroxide are used in the United States. The first and most important is the Deguide process for converting barium carbonate to the hydroxide via barium silicate. With this process, the Great Western Sugar Co. of Denver, Colo., makes its barium hydroxide used in the clarification of beet sugar juice. The Deguide process is discussed under witherite (p. 56). The other process is the simple slaking of barium oxide with water.[99]

Some of the other processes that have been proposed are listed in the footnote;[100] some appear to have merit.

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[96] Fleck, H., Process of Oxidizing Barium Monoxid to Dioxid: U. S. Patent 1,349,417, Aug. 10, 1920.

[97] Brin, A., Process of Making Barium dioxide: U. S. Patent 359,423, Mar. 15, 1887. ($Ba(NO_3)_2$ heated to BaO, then air admitted to form BaO_2.)

[98] Jaubert, G. F., Process of Making Hydrates of Alkaline Earth Dioxides: U. S. Patent 734,713, July 28, 1903. (BaS solution reacted with NaO_2.)
Blackmore, H. S., Process of Making Nitric or Other Oxynitrogen Acid and Metal Peroxid: U. S. Patent 982,466, Jan. 24, 1911. ($Ba(NO_3)_2$ + superheated steam + O_2 from air, under pressure $\longrightarrow BaO_2$.)
Bergius, F., Process of Making Alkali-earth Peroxid: U. S. Patent 1,015,286, Jan. 23, 1912. (O_2 gas bubbled through BaO-NaOH melt to form BaO_2.)
Jewell A. J., Process and Apparatus for the Production of Barium Peroxide: U. S. Patent 1,433,377, Dec. 12, 1922. (Hydrated barium hydroxide dispersed in droplets into heated oxygenating atmosphere to yield BaO_2.)

[99] Refinements in the process have been patented by Windecker, R. E., Manufacture of Barium Hydrate: U. S. Patents 2,016,529-30, Oct. 8, 1935.

[100] Jahn, F., Process of Manufacturing Hydrates of Alkalies and Alkali Earths: U. S. Patent 744,920, Nov. 24, 1903. (Electrolysis of solution of BaS with iron anode to combine with S liberated. $Ba(OH)_2$ crystallizes from cooled solution.)
Barnes, E. A., Process of Preparing Barium Hydroxid from Barium Sulfide: U. S. Patent 1,316,133, Sept. 16, 1919. (Cooling BaS solution until $Ba(OH)_2 \cdot 8H_2O$ crystallizes out.)
Stuer, B. S., Manufacture of Barium Hydroxide and Strontium Hydroxide: U. S. Patent 1,812,250, June 30, 1931., (NaOH + BaS in NH_4OH solution $\longrightarrow Ba(OH_2)$.
Mertes, A. T., Barium Hydroxide Production: U. S. Patent 2,173,912, Sept. 26, 1939. (BaS + ZnO in water with heat and pressure yields $Ba(OH)_2$ and ZnS.)

Barium nitrate. - There are three general processes of making barium nitrate. The one in general use involves the digestion of barium carbonate (either witherite or precipitated carbonate) with commercial calcium nitrate (80 percent pure).[101] Calcium carbonate, being less soluble than barium carbonate, precipitates and is separated from the hot solution of barium nitrate, which is allowed to crystallize. Another method involving a reagent more expensive than calcium nitrate is the reaction of barium sulfide solution with aluminum nitrate according to the following idealized equation: $3BaS + 2Al(NO_3)_3 + 6H_2O \rightarrow 3Ba(NO_3)_2 + 2Al(OH)_3 + 3H_2S$.[102] The aluminum hydroxide floc is settled and separated, and barium nitrate is crystallized from solution. Another general method is differential crystallization of a barium salt such as barium chloride with sodium nitrate. This has been used in Germany and England in earlier years.[103]

It is doubtful that black ash leach liquor could be treated with nitric acid to yield barium nitrate and hydrogen sulfide, owing to the oxidation of sulfide ions to sulfate followed by precipitation of barium sulfate.

BARIUM CHEMICALS - USES

Blanc Fixe

Precipitated barium sulfate, blanc fixe, is used as a base or extender in vehicles of high refractive index (such as the usual drying oils) and as a pigment in vehicles of low refractive index (such as water paints). It may be used as a base for the precipitation of titanium dioxide for organic dyes (lakes). In making barium-base titanium pigments, titanium dioxide may be precipitated directly on a barium sulfide nucleus, or the dry materials may be intimately mixed.[104] In any event the pigment generally contains about 30 percent TiO_2 and 70 percent $BaSO_4$.

In the precipitation process, clarified ilmenite liquor (ilmenite dissolved in sulfuric acid) is hydrolyzed by boiling, and TiO_2 (anatase) precipitates on the surfaces of the blanc fixe nuclei. The precipitate is filtered, dried, brought to red heat, cooled, ground, and bagged.

Blanc fixe is difficult to redisperse in water after once having been dried, and for this reason much of it is sold in a pulp containing 20 to 30 percent water. Pulp blanc fixe is used mostly as a paper filler. Sales of dry blanc fixe for use in paints, printing, rubber, linoleum, and oilcloth are somewhat smaller.

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[101] Wilson, N. R., Process of Producing Barium Nitrate: U. S. Patent 2,010,046, Aug. 6, 1935.

[102] Davis, R. W., Jr., Manufacture of Alkali Earth Nitrates and Hydrogen Sulfide: U. S. Patent 1,321,013, Nov. 4, 1919.

[103] Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 3, 1923, p. 849.

[104] An interesting review of the various methods of making barium sulfates and evaluations of their characteristics for use in mechanical mixtures of barium-base titanium pigments is given by Booge, J. E., Blended Pigment: U. S. Patent 2,046,054, June 30, 1936.

Barium sulfate may be precipitated in leather by soaking the leather in a solution of a soluble barium salt, generally barium chloride, then removing it and soaking it in another vat containing a soluble sulfate, generally sodium sulfate. This process is widely used in making white kid leathers.

According to Dawson,[105] blanc fixe decreases the time required for rubber-sulfur mixtures to reach their maximum tensile strength, and the finer the powder the greater this accelerating action. Blanc fixe reenforces rubber up to a certain volume, but further addition decreases the rubber quality.

Barium Chloride

Barium chloride is used in case-hardening (see pp. 45-46), as a mordant in textiles, in forming blanc fixe in place in leather and cloth, as a flux in making magnesium metal, and in numerous chemical processes. Like other soluble barium compounds, it may be used in descumming brick and in removing sulfate ions from water.

Barium Carbonate

Outside the barium industry, most barium carbonate is used normally to prevent the formation of scum in ceramics exposed to moisture. In most ceramics there are small percentages of relatively soluble sulfates, mostly calcium, which are dissolved from the body of the ceramic and remain as a scum on the surface after the product has been wetted. If a little barium carbonate is mixed in the ceramic batch, the following reaction occurs: $BaCO_3 + CaSO_4 \longrightarrow BaSO_4 + CaCO_3$. As each end product is respectively less soluble than either reactant, sulfates are not leached out of the ceramic.[106]

Besides preventing scumming in ceramics, barium carbonate is also said to diminish porosity and prevent discoloration of brick. By applying it on the surface after firing, a resistant and brilliant glaze is obtained.[107]

Probably the most important direct wartime use of barium carbonate is in salt baths for case-hardening bomb shells, tools, and other steel parts. Before the war, witherite, being less costly, was employed for this purpose rather than precipitated barium carbonate; however, reduced imports of witherite have broadened, at least temporarily, the demand for the synthetic material. The action of barium carbonate as a carbon carrier in steel hardening is not precisely known, but when it is mixed with powdered coke and heated with iron parts at 1,700° F., the coke is gradually oxidized and the carbon content of the surface grains of the iron is increased, thus case-hardening the product. Other barium compounds, notably barium peroxide, are said to be capable of similar use. Case-hardening is discussed in more detail on pp. 43-46.

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[105] Dawson, T. R., Barytes and Its Employment in the Rubber Industry: India Rubber Jour., vol. 73, 1927, pp. 885-889, 926-930, 961-966.

[106] See a trade bulletin, The Manufacture of Brick Using Barium Carbonate, published by the Grasselli Chemical Co., Inc. (now E. I. DuPont de Nemours & Co.) in 1933, 40 pp.

[107] Verre & Silicates, Inc., Employing Precipitated Barium Carbonate in Ceramics, vol. 5, No. 5, 1934, p. 94. Jour. Amer. Ceram. Soc. (Ceram. Abs.), vol. 13, No. 7, July 1934, p. 193.

Considerable barium carbonate is used in making optical glasses. Ordinary soda glass is made by melting together sand, limestone, and soda ash at about 1,375° C., so that sodium-calcium silicate (glass) is formed. When a substantial amount of barium carbonate is added to the ingredients mentioned, the resultant glass has greater refraction, higher luster, and a full ringing tone. The disadvantages are greater weight and less toughness. (The decreased toughness, on addition of considerable amounts of BaO in the batch, is not to be confused with the slightly greater toughness imparted by only a small amount of BaO, as for example when barite is added to continuous melts as a surface flux.)

Barium carbonate is used in making both of the two main types of optical glasses - crown and flint. Light dispersion is eliminated by proper combination of these two types of lenses. The term "crown" was originally confined to alkali-lime-silica glasses, and the name "flint" to alkali-lead oxide-silica glasses. Substitution of barium oxide for lime in crown glass gives a "barium crown", and if barium oxide replaces lead oxide in flints the glass is called a "barium flint".

Some optical glasses contain nearly half their weight as BaO; for example, the following dense barium crown glass: BaO, 48.7 percent; SiO_2, 31.3; B_2O_3, 15.4; Al_2O_3, 3.5; K_2O, 0.2; CaO, 0.2; Sb_2O_3, 0.4; and As_2O_3, 0.2 percent.108/

Barium carbonate has been used in Germany in enamels as a substitute for borax.109/ It is recommended that the carbonate be dry, finely ground, and intimately mixed. The material treated with the carbonate should be stored for at least 6 days, so that the carbonate will have time to act and transform all soluble sulfate into insoluble salts.110/

Barium carbonate may be used in place of the more expensive barium hydroxide in removing sulfate ions from boiler-water feed if lime water is added to the feed with the carbonate.111/

Pierce has prepared a highly reactive barium carbonate that can be used in brine purification to remove virtually all Ca, Mg, and SO_4 ions.112/

108/ Settlingstones Mines, Ltd., Sales Agents, J. Cameron Swan & Co., Ltd., 4 St. Nicholas Bldgs., Newcastle-upon-Tyne 1, Great Britain, Witherite (Natural Barium Carbonate) and Its Industrial Uses: 1940, 56 pp., (at p. 37).

109/ Beneschovsky, F., Barium-containing Enamels and Their Toxicity: Keram. Rundschau, vol. 49, No. 1, 1941, pp. 5-7. Ceram. Abs., vol. 20, No. 11, November 1941, pp. 259-60.
Vielhaber, L., Barium Oxide as Enamel Raw Material: Emailwaren-Ind., vol. 17, pp. 87-90, 93-95 (1940); Chem. Abs., vol. 35, No. 6, March 20, 1941, p. 1956.

110/ Avenhaus, W., Technique of Barium Addition: Tonind. Ztg., vol. 60, 1936, pp. 551-53; Ceram. Abs., vol. 16, No. 1, Jan. 1937, p. 50.

111/ Rodman, C. J., Water Softening with Barium Salts: Chem. and Met. Eng. vol. 35, No. 4, April 1928, pp. 221-223.

112/ Pierce, J. B., Jr., Method of Purifying Brines: U. S. Patent 2,191,411, Feb. 20, 1940.

A relatively new use of $BaCO_3$ is in drilling oil wells. In drilling through gypsum-bearing formations, the drilling mud tends to be flocculated by dissolved $CaSO_4$. The $BaCO_3$ present reacts to form less soluble $CaCO_3$ and $BaSO_4$.

Barium carbonate also has been recommended as rat poison[113] and an insecticide.[114]

Barium Oxide and Peroxide

Prior to development of electrolytic methods, the only commercial method of making hydrogen peroxide was by treating barium peroxide with sulfuric acid, which process gave precipitated barium sulfate as a byproduct. A small share of the hydrogen peroxide market is retained by barium chemical manufacturers, but the future of BaO_2 appears to depend on uses for its dry powdered form, particularly in bleaches. Before oxygen became available by fractional distillation of liquid air, one of its main sources was barium peroxide, through the Brin process. BaO was heated to 450° C., when it took up O_2 from the air to form BaO_2. On heating to higher temperatures, oxygen was released.

A mixture of barium oxide and witherite added to electric-furnace heats of ferrous metals half an hour before pouring is said to increase the life of the acid lining of the furnace, produce a quieter and steadier arc, and reduce sulfur content and slag viscosity.[115]

Barium oxide in glass is said to increase refractive index, density, and elasticity.[116] However, barium probably can be added to the glass batch in several forms cheaper than the powdered oxide, namely as glass-grade barite, witherite, or precipitated barium carbonate. (See p. 23 on the use of barite in glass.)

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[113] See footnote 108 (p. 39). Schwartze, E. W.; Toxicity of Barium Carbonate to Rats; Dept. Agric. Bull. 915, 1920, 11 pp.

[114] Bull. Imperial Institute, Barium Carbonate as an Insecticide: Vol. 35, No. 1, January -March 1937, p. 81.

[115] Baernstein, M. A., A New Electric Furnace Technique: The Use of Barium Flux, Metal Ind., vol. 32, No. 10, 1940, p. 338.

[116] Pottery Gazette, Barium and Magnesium Oxides as Glass-forming Oxides: Vol. 58, No. 676, 1933, p. 1252. Ceram. Abs., vol. 12, No. 12, Dec. 1933, p. 417.

Wessels, Vincent E., Effects of Replacing Dolomitic Lime by Baryta upon Some Properties of Glass: Bull. Am. Ceram. Soc., vol. 15, No. 3, March 1936, p. 82.

Kamp, K., Barium and Zinc Oxides in Enamel: Glashuette, vol. 64, No. 44, 1934, pp. 715-717. Jour. Amer. Ceram. Soc. (Ceram. Abs.), vol. 14, No. 5, May 1935, p. 108.

Barium Hydroxide

Like barium carbonate and chloride, barium hydroxide is used to prevent scumming of ceramic products.[117]

Residual beet-sugar molasses from the Steffens process[118] contains sugar, which may be recovered by means of the barium saccharate process, as practiced by Great Western Sugar Co., Denver, Colo. Barium hydroxide is added to the discard molasses, and the group $Ba(OH)^+$ displaces a hydrogen-ion from one of the hydroxyl groups of sucrose, yielding insoluble monobarium saccharate and water. The monobarium saccharate is filtered, suspended in water, and carbonated to yield a precipitate of barium carbonate and a solution of pure sugar. The carbonate is filtered off for use in making more barium hydroxide, and the sugar solution is worked up in multiple-effect evaporators.

Barium Nitrate

Production of barium nitrate, normally only a few tons a year in peacetime, is much greater in wartime because of its use in green signal flares and in primers and detonators.

Barium nitrate is a convenient source of BaO for enamel frits, and is said to be superior to nitrates of the alkali metals because it is less soluble and hence less liable to attack the walls of the fusion vessel. Also, the decolorizing action of barium nitrate is said to be better than that of the alkali nitrates. The frits obtained powder easily.[119] Barium nitrate may replace a part of minium in enamel frits.[120]

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[117] Everhart, J. O., Rueckel, W. C., and Austin, C. R., Barium Hydroxide to Prevent Scumming of Ceramic Products: Ohio State Univ. Studies, eng. ser., 1934, 3 (5. part 1). Eng. Expt. Sta. Circ. No. 30, Building Sci. Abs., vol. 8 (N.S.), No. 7, July 1935, p. 218.

[118] See Riegel, E. R., Industrial Chemistry, 4th ed., pp. 412-413, for a description of the Steffens process.

[119] Chemical Industries, Barium Nitrate in Enamel Frits: Vol. 34, No. 5, May 1934, p. 419.

[120] Grote, T. G., Barium Nitrate in the Production of Enamels and Glazes: Glashuette, vol. 63, No. 29, 1933 pp. 492-94; vol. 63, No. 30, 1933, pp. 507-508; abstracted in Emailwaren-Ind., vol. 11, No. 1, 1934, p. 7. Jour. Am. Ceram. Soc. (Ceram. Abs.), vol. 13, No. 5, May 1931, p. 110.
---------------, Barium Nitrate as Enamel Raw Material: Glashuette, vol. 63, No. 47, 1933, pp. 796-97; Jour. Am. Ceram. Soc. (Ceram. Abs.), vol. 13, No. 7, July 1934, p. 171.
Glashuette, Barium Nitrate as Enamel Raw Material: Vol. 63, No. 42, 1933, p. 696. Jour. Am. Ceram. Soc. (Ceram. Abs.), vol. 13, No. 6, June 1934, p. 142.

Barium Metal

Metallic barium has been shown to be a satisfactory deoxidizer of copper, and because of its limited solubility in copper, Ba decreases its conductivity but little.[121] Barium metal has a high rate of electron emission when subjected to an electric potential, and this property is utilized in alloys for spark plugs and electron-emission elements in electron tubes.[122]

Lead hardened with barium metal has been proposed as a bearing metal; it is said that high compression strength and hardness of the alloy are satisfactory, but that load-carrying capacity and action under high speeds are not so good as tin-base alloys.[123]

Miscellaneous Barium Chemicals

Barium tungstate, molybdate, and chromate (lemon yellow) are used to some extent as paint pigments.[124] Barium silicofluoride is said to be useful in the control of corn worm.[125] Barium aluminate and sodium barium aluminate are used to remove magnesium ions as insoluble magnesium aluminate in water softening. Barium nitrophthalate has been used in Germany to protect iron work from rust.[126]

Barium acetate is used as a textile mordant; barium chlorate in explosives, pyrotechnics, and as a textile mordant; barium chromate in safety matches and as an oxidizing agent in explosives; barium cyanide in metallurgy; barium ethyl sulfate in organic syntheses; barium fluoride in enamels, antiseptics, and embalming fluids; barium manganate as a pigment; and barium sulfide as a depilatory and in vulcanizing. Various barium compounds have been used as electron-emission surfaces in electron tubes.

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[121] Schumacher, E. E., and Ellis, W. C., The Deoxidation of Copper with the Metallic Deoxidizers Calcium, Zinc, Beryllium, Barium, Strontium, and Lithium: The Metal Industry (London), vol. 40, No. 20, May 13, 1932, pp. 517-520. Abstracted in Chemistry and Industry (London), vol. 51, No. 40, Sept. 30, 1932, p. 844.

[122] Duffendack, O. S., Wolfe, R. A., and Randolph, D. W., The Development of an Electron-Emitting Alloy: The Metal Industry, vol. 38, No. 21, May 22, 1931, pp. 527-528.

[123] Grant, Leland, Bearing Metals of Lead Hardened with Alkali and Alkaline Earth Metals: Metals and Alloys, vol. 5, August 1934, pp. 161-164; September 1934, pp. 191-195; vol. 6, No. 2, February 1935, p. 79.

[124] Lembrecht, W., Barium Pigments: Paint and Varnish Production Manager, vol. 21, pp. 104-5 (1941). Chem. Abs., vol. 35, No. 11, June 10, 1941, p. 3835.

[125] Chemical Markets, Barium Silicofluoride: Vol. 33, No. 1, July 1933, p. 55.

[126] Chemical and Metallurgical Engineering, vol. 49, No. 9, September 1942, p. 170.

Barium Compounds in Carburizing Steel

There are three general methods of carburizing iron or steel - with carbon-bearing vapors, with solid carbonaceous material, and with molten salts containing carbon or a compound of carbon. Barium compounds are used extensively in the last two processes.

Case-hardening with solid carburizers is really a subdivision of vapor carburization, for the carbon is introduced into the iron or steel by means of CO gas. There is believed to be no direct action of the charcoal in the carburizer on the iron, for when the iron articles are packed in pure carbon, such as pure charcoal or pure graphite, no case-hardening results. However, when an "energizer" such as $BaCO_3$ is added to the charcoal, case-hardening proceeds satisfactorily. Early theories on the action of $BaCO_3$ were to the effect that it dissociated at carburization temperatures, giving $BaO + CO_2$. The carbon dioxide reacted with charcoal, giving CO. Carbon monoxide reacted with iron to give Fe_3C and CO_2. The CO_2 reacted with more C to give more CO, and so on. This view received a serious jolt when it was found that BaO was just as effective as $BaCO_3$ as an "energizer," and the prevalent view now is that all oxygen needed for the formation of CO and CO_2 is obtained from adsorbed films on the charcoal, and that BaO is purely a catalyst. This proposition is supported by the fact that when the carburizing pack becomes exhausted, it can be regenerated by exposure to air. This procedure permits the charcoal to readsorb air. According to early theory, $BaCO_3$ was superior to calcium and sodium carbonate because the two latter carbonates released all their CO_2 before carburization temperature was reached. But is now seems impossible to explain the superiority of $BaCO_3$ on this ground, in view of the fact that BaO is equally effective. However, the general impression is that sodium and calcium carbonates aid at least in the first stages of carburization, while the box is being brought up to heat, and on this theory small quantities of both may be incorporated in the carburizing compound, somewhat as follows: Hardwood charcoal, 53 to 55 percent; coke, 30 to 32, sodium carbonate, 2 to 3; precipitated barium carbonate, 10 to 12; and calcium carbonate (whiting), 3 to 4 percent. The materials are impregnated with a tacky binder such as molasses, pelletized to pea size in a mechanical shaker, and coked.

The process of box carburizing is carried on somewhat as follows: A layer of pellets is laid in the box, which is generally an alloy steel, and the articles are placed carefully on this layer so that they do not touch. Pellets are then packed around and over the articles, a sheet of cardboard is laid down, and the process is repeated until the box is filled, after which the lid is sealed on with clay. The boxes are placed in a furnace and heated to the desired temperature, which may vary from 1,650° to 1,750° F. but typically is 1,700° F. Heat is applied for a few hours to a few days, depending on the depth of case desired, and then the boxes are removed and the articles quenched or cooled slowly, depending on the grain structure sought.

Although most proprietary carburizing compounds contain precipitated barium carbonate, satisfactory results may be obtained with fine-ground witherite, according to Noy and Bliss.127/

127/ Noy, J. M., and Bliss, L. G., Witherite in Case Hardening: Foote-Prints, vol. 12, No. 2, December 1939, pp. 15-26.

Excellent general references on box carburizing are given in a footnote.[128]

Carbon suspended in fused sodium chloride baths has been used since the Middle Ages or before to case-harden files, chisels, axes, and other steel articles. For a long time it was thought that the salt itself was the active agent, and not until comparatively recently was carbon recognized as the true hardener, forming Fe_3C. Later, a bath of potassium cyanide (soon superseded by cheaper NaCN) was used as a source of carbon, but it was found that the lone salt was corrosive and that the bath became inactive after its content of sodium carbonate (a reaction product) became sufficiently great. These difficulties were overcome by diluting the sodium cyanide with other feasible but less corrosive salts, principally barium chloride. This salt seemed particularly useful in carburizing at temperatures around 2,000° F.

Considerable research in carburizing salt baths was carried on in the 1920's and increased through the thirties.

A certain amount of oxidation of the steel articles occurs in barium chloride baths, yielding iron oxide, which reacts with iron carbide in the steel, pitting it. Dean[129] suggested adding aluminum to the bath to prevent pitting, on the theory that the aluminum would reduce iron oxide to metallic iron, which would alloy with aluminum. Also see High's patent (footnote 140) for a method of preventing oxidation of the bath by precipitating carbon, which rises to the surface and forms a protective layer.

Kuenrich[130] proposed a bath consisting of 95 percent $BaCl_2$ and 5 percent of a mixture of equal parts of calcium borate, potassium carbonate, and potassium ferrocyanide or cyanide. Early workers on the subject appeared to regard the utility of the barium salt limited to its character as an inert vehicle or solvent.

Lower heat-treating temperatures (960° C. and below) were obtained by adding potassium or sodium chlorides to the bath, as proposed by Harding and Holt.[131] The suggested composition of such a bath was 30 to 60 percent $BaCl_2$, 10 to 20 percent NaCN, and remainder alkali metal chlorides.

One of the first mentions of the use of $BaCO_3$ in salt baths is made in Malcolm's patent,[132] wherein a bath composed of potassium carbonate, soda ash, barium carbonate, potassium cyanide, and sodium cyanide is proposed, with specified proportions. Beck[133] also used $BaCO_3$ in small quantities, but his main vehicle was a mixture of barium and strontium chlorides. The bath was compounded as follows: 60 percent $BaCl_2$, 12 percent NaCN, 8 percent KCl, 1 percent NaCl, 15 percent $SrCl_2$, and 3 percent $BaCO_3$. The specification reads:

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[128] Carburizing. A symposium published by the American Society for Metals in 1938, 339 pp.
Bullens, D. K., Steel and Its Heat Treatment: 4th ed., vol. 1, 1938, 445 pp.

[129] Dean, R. S., Fused Salt Bath for Heating Steel in Hardening: U. S. Patent 1,454,214, May 8, 1923.

[130] Kuenrich, P. R., Manufacture of Steel: U. S. Patent 1,520,063, Dec. 23, 1924.

[131] Harding, E. A., and Holt, D. A., Process and Composition for Treating Metals: U. S. Patent 1,970,852, Aug. 21, 1934.

[132] Malcolm, V. T., Method of Hardening Steel: U. S. Patent 1,967,994, July 24, 1934.

[133] Beck, W., Fused Bath for Carburizing Iron, Steel, and the Like: U. S. Patent 1,980,152, Nov. 6, 1934.

> After immersion for 2 hours at 930° C., the carburizing depth hardened is about 1 mm.; after 4 hours about 1.4 to 1.6 mm., and after 6 hours about 1.8 to 3.0 mm. The hardened surface after quenching in cold water is about 60° to 65° Rockwell.

Beck later found that decomposition of the bath could be delayed by raising the $BaCO_3$ content to between 5 and 10 percent.[134] Then the inventor discovered that BaO and $BaCO_3$ built up in the bath and halted carburization in an unknown manner. He proposed to maintain the $BaCO_3$ content of the bath at the optimum by a daily addition of a mixture of 1 part $SrCl_2$ and 7 parts $BaCl_2$, the quantity added being 3 to 5 percent of the weight of the bath. He gave a typical bath, where such renewal proved efficacious as 50 percent $BaCl_2$, 25 NaCl, 25 KCl, and 5 to 10 percent NaCN, and noted that the renewal was more effective by addition of mixed Sr and Ba chlorides than by either alone.[135]

Baths in which barium chloride has been the principal constituent have been found adaptable to carburizing agents other than the cyanides. Albrecht[136] proposed that the main carburizing agent be finely divided carbon suspended in a bath of $CaCl_2$ containing 3 percent NaCN. High[137] suggested "activated carbon of low combustibility." Hanusch[138] proposed graphitic acid in the following bath: $BaCl_2$, 68 percent; NaCN, 8; NaCl, 17; graphitic acid ($C_{11}O_4$), 2; and $BaCO_3$, 5.

Holden[139] was one of the first to suggest that a barium salt might be more than merely an inert solvent for NaCN. His bath consisted of NaCN, 45.9 percent; $BaCl_2$, 31.1; NaF, 12.4; and CaF_2, 7.3. According to the specification, "*** the $BaCl_2$ in conjunction with the NaCN tends to increase the nascent C, which is operative for penetration." (A more definite theory of how such nascent carbon was produced - through an intermediate BaO or $BaCO_3$ step - was proposed later by High.[140] Another novel idea in Holden's patent was the use of NaF to render the "drag-out" film of fused salts more easily soluble in water, facilitating its removal.

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[134] Beck, W., Method of Case-hardening Articles: U. S. Patent 1,993,204, Mar. 5, 1935.

[135] Beck, W., Method of Case-hardening Iron Articles: U. S. Patent 1,996,269, April 2, 1935.

[136] Albrecht, C., Process for Carburizing and Hardening: U. S. Patent 2,007,136, July 2, 1935.

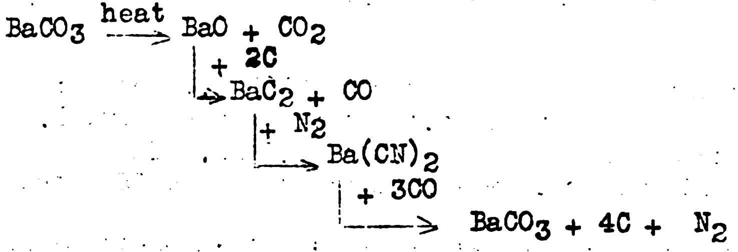
[137] High, H. H., Salt Bath for Carburizing and Method of Carburizing: U. S. Patent 2,078,244, April 27, 1937.

[138] Hanusch, H., Iron and Steel Cementing Bath Composition: U. S. Patent 2,095,188, Oct. 5, 1937.

[139] Holden, A. F., Composition for Case-hardening: U. S. Patent 2,046,822, July 7, 1936.

[140] High, H. H., Salt Bath for Carburizing and Method of Carburizing: U. S. Patent 2,078,244, April 27, 1937.

High (work cited in previous footnote) suggests that if sufficiently large quantities of $BaCO_3$ or BaO are used, the retardation effect of BaO (patented by Beck)[134] is supplanted by the following reactions:



$$BaCO_3 \xrightarrow{heat} BaO + CO_2$$
$$BaO + 2C \rightarrow BaC_2 + CO$$
$$BaC_2 + N_2 \rightarrow Ba(CN)_2$$
$$Ba(CN)_2 + 3CO \rightarrow BaCO_3 + 4C + N_2$$

A thick layer of carbon precipitates and covers the surface of the bath, preventing oxidation. According to this theory, considerable nascent carbon is made available for use either in carburization or for recycling in the series of reactions, and carburization is said to be speeded and bath decomposition to be inhibited. Carbon is replenished by addition of NaCN and activated carbon of low combustibility. The NaCN content should not fall below 10 percent. The preferable composition of the bath is given as NaCN, 15 percent; $BaCO_3$, 25; $BaCl_2$, 29; NaCl, 26; and activated carbon, 5 percent.

Noncarburizing baths also may use $BaCl_2$ when cementation is not desired, but merely uniform heat treatment. Holt[141] suggests the following bath for this purpose (especially for strip steel): NaCN, 2 to 20 percent, the remainder being the mixture $BaCl_2$, 50 percent; KCl, 30; and NaCl, 20. Solakian and Case[142] proposed the following as an efficacious high-temperature (about 2,350° F.) hardening bath in an electric furnace: $BaCl_2$, 75 percent; BaF_2, 10; and CaF_2, 15 percent. It is claimed that the bath does not change carbon content of the articles treated. Bonath and Albrecht[143] developed a salt bath for heat-treating aluminum alloys without corroding the alloy or changing its composition, as follows: KCl, 25 to 45 percent; NaCl, 15 to 25; $CaCl_2$, 10 to 20; $BaCl_2$, 10 to 20; $SrCl_2$, 5 to 20; $BaCO_3$, 1 to 25 percent.

PRICES

The price of crude barite has varied over a wide range, depending on time and place. In Missouri, for example, the price per short ton of crude barite was $7 in 1860,[144] $10 in 1868,[144] $8 in 1882,[145] and $5 in 1890.[145] Later prices in Missouri and on the Atlantic coast (as exemplified by Virginia, 1901-1908, and Georgia, 1911-1944) are given in an accompanying table. Fluctuations caused by the first World War and the depression of the thirties will be noted. Such a table cannot show price extremes, which have been lower than $2 and higher than $18 a short ton.

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[141] Holt, D., Heat-Treating Process: U. S. Patent 2,231,009, Feb. 11, 1941.

[142] Solakian, H., and Case, E., Method of Treating High-Speed Steel: U. S. Patent 2,349,767, May 23, 1944.

[143] Bonath, K., and Albrecht, C., Process for the Thermal Treatment of Light Metals and Light-Metal Alloys: U. S. Patent 2,066,454, Jan. 5, 1937.

[144] Photostat records furnished by A. H. Long, Potosi, Mo.

[145] Geological Survey, Mineral Resources of the United States.

Average price of crude barite in Missouri and on the Atlantic coast per short ton at mine, 1901-1944

(From Mineral Resources, 1901-1931, Minerals Yearbook, 1932-1944, and some previously unpublished records of the Department of Interior.)

Year	Missouri	Atlantic coast		Year	Missouri	Atlantic coast	
1901	$3.52	$3.05	(Va.)	1923	$7.70	$8.05	(Ga.)
1902	3.35	3.20	do.	1924	7.83	8.00	do.
1903	3.35	3.58	do.	1925	7.87	7.21	do.
1904	3.00	2.81	do.	1926	7.96	6.86	do.
1905	3.14	2.78	do.	1927	7.15	6.17	do.
1906	3.23	3.84	do.	1928	7.09	6.01	do.
1907	3.69	3.55	do.	1929	7.42	5.80	do.
1908	3.48	4.55	do.	1930	7.08	5.53	do.
1909	3.44	Data not available		1931	5.77	5.30	do.
1910	3.33		do.	1932	5.42	6.42	do.
1911	3.79	3.00	(Ga.)	1933	4.54	6.55	do.
1912	4.77	3.55	do.	1934	4.90	6.41	do.
1913	3.78	3.55	do.	1935	5.52	5.83	do.
1914	3.37	3.64	do.	1936	6.27	5.37	do.
1915	4.05	3.31	do.	1937	7.22	5.36	do.
1916	6.27	3.83	do.	1938	7.36	4.90	do.
1917	6.63	5.41	do.	1939	6.78	5.06	do.
1918	8.02	6.03	do.	1940	6.78	5.04	do.
1919	8.74	7.83	do.	1941	6.30	5.30	do.
1920	10.17	9.34	do.	1942	6.44	5.58	do.
1921	8.65	7.78	do.	1943	7.20	6.28	do.
1922	6.35	8.21	do.	1944	7.44	8.54	do.

There are several purchasing arrangements. Many of the Missouri washers sell to National Lead Co. at a flat rate of $8.50 a short ton delivered Fountain Farm, Mo. Five percent moisture is assumed to be present (it may be more in winter, less in summer), and $0.425 per ton is subtracted for moisture content. Some of the Missouri washers sell to lithopone and chemical manufacturers on a premium-penalty basis, receiving $8.50 for material analyzing 94 percent barium sulfate and 1 percent iron oxide. Twenty-five cents a ton additional is paid for each percent of barium sulfate over 94 and subtracted for each percent less than 94. However, barite analyzing less than 92 percent barium sulfate is generally not accepted, even on a penalty basis, for chemical of lithopone use. For each 0.1 percent iron oxide less than 1 percent, 25 cents a ton is added; and for each 0.1 percent iron oxide more than 1, 25 cents is deducted. Thus, the theoretical maximum price obtainable for Missouri barite (100 percent pure) is $12.50 a short ton. Missouri prices frozen by Office of Price Administration as of the highest price in March 1942 were about $7 a short ton, which ceiling was raised to $8.50 July 26, 1944. Prices frozen in Georgia and Tennessee were $8 to $8.50 a long ton, and on April 8, 1944, increases were permitted enabling producers to sell at $9.50 to $11 a long ton, depending on the individual ceilings established by the Office of Price Administration. The premium-penalty system is not used as much in Georgia and Tennessee as in Missouri.

The method of analysis of barite may have a considerable effect upon the price charged for it, particularly in the premium-penalty system. Lithopone makers frequently include strontium with barium if the former is not excessive (perhaps 1 percent or less), for a small quantity of strontium is not objectionable in lithopone. Some buyers analyze and pay for the total barium content, whereas others pay on a basis only of the barium present as sulfate. The latter procedure is not unfair, for only the sulfate of barium reacts to yield black ash. Any barium present as carbonate is merely a diluent.

MARKETING AREAS

There are three general marketing areas, which arbitrarily may be named the Pacific, Central, and Eastern districts. Barite produced in California and Nevada is consumed chiefly in California for well drilling, lithopone, and barium chemicals. The Pacific area is largely self-contained. In the Central area the producing States are Missouri and Arkansas. Arkansas barite is sold almost entirely for use in well drilling in the Gulf area, although some has been sold for glass making in West Virginia, Ohio, Illinois, and other States. Missouri barite is consumed in well drilling in the Gulf area, in making bleached ground barite and titanium pigments in St. Louis, and barium chemicals and lithopone in Illinois and Kansas. In the absence of cheap barite imported from Germany, nearly all barite mined in Georgia and Tennessee is consumed in chemicals in West Virginia and in chemical and lithopone plants on the Atlantic coast. Prior to 1939, competition with German barite in Atlantic coast markets forced Tennessee and Georgia barite to compete with Missouri barite for lithopone markets in Illinois. In this way, German barite influences the Central market.

The appended table shows freight rates between principal points of supply and demand.

Costs of delivering a short ton of chemical-grade barite to certain cities in the United States, July 1944

(Unloading and handling charges and insurance are not included on the ocean shipments. The unloading and handling charge on Nova Scotia barite received at Baltimore is $1.13, insurance is $0.03, and miscellaneous, $0.35.)

To -	From -				
	Cartersville, Ga.	Sweetwater, Tenn.	St. Louis, Mo.	Germany (prewar rates)	Nova Scotia
Charleston or Huntington, W. Va.:					
F.o.b. origin..	1/$8.93	1/$8.93	1/$8.50	$5.30	$6.82
Freight........	3.93	3.54	5.20	2/9.86	3/9.38
Duty...........	-	-	-	3.57	3.57
	12.86	12.47	13.70	18.73	19.77
Palmerton, Pa.:					
F.o.b. origin..	1/8.93	1/8.93	1/8.50	5.30	6.82
Freight........	5.40	4.91	5.36	4/6.21	5/5.07
Duty...........	-	-	-	3.57	3.57
	14.33	13.84	13.86	15.08	15.46
Baltimore, Md.:					
F.o.b. origin..	1/8.93	1/8.93	1/8.50	5.30	6.82
Freight........	4.32	3.83	5.36	3.86	6/3.38
Duty...........	-	-	-	3.57	3.57
	13.25	12.76	13.86	12.73	13.77
Grasselli, N. J.:					
F.o.b. origin..	1/8.93	1/8.93	1/8.50	5.30	6.82
Freight........	5.89	5.22	6.38	3.86	7/2.72
Duty...........	-	-	-	3.57	3.57
	14.82	14.15	14.88	12.73	13.11
Newport, Del.:					
F.o.b. origin..	1/8.93	1/8.93	1/8.50	5.30	6.82
Freight........	4.50	4.42	5.36	3.86	7/3.38
Duty...........	-	-	-	3.57	3.57
	13.43	13.35	13.86	12.73	13.77
Chicago, Argo, and Depue, Ill.:					
F.o.b. origin..	8.93	8.93	8.50	8/	8/
Freight........	5.05	5.05	3.20	-	-
	13.98	13.98	11.70		

1/ Cheapest ceiling rate. In Georgia and Tennessee, considerable barite was also sold at ceilings of $9.38 and $9.82.

2/ Ocean rate is $3.86; nominal freight, Baltimore to Charleston, is $6.00.

3/ Ocean rate is $3.38; nominal freight, Baltimore to Charleston, is $6.00.

4/ Ocean rate is $3.86; freight, New York to Palmerton, is $2.35.

5/ Ocean rate, full cargo, $2.72, including 13 percent surcharge; freight, New York to Palmerton, is $2.35.

6/ Full cargo rate; includes 22 percent surcharge.

7/ Full cargo rate; includes 13 percent surcharge.

8/ Competition is out of the question.

TARIFF HISTORY

Barite has been dutiable since the Tariff Act of 1883, with the exception of the period covered by the Act of 1894, when crude barite was free. Witherite has been exempt from duty since 1883. The trade agreement with Cuba in 1939 provides that Cuban crude barite is subject to a duty of $3.20 a long ton (as compared with $4 for barite originating in other countries).

Duties levied on barite, manufactured and unmanufactured (meaning ground or crude), and provisions for witherite, Acts of 1883 to 1930.

Act of –	Paragraph	Tariff classification	Rates of duty (all tons are 2,240 pounds)
1883	40	Baryta, sulfate of, or barytes, unmanufactured	10 percent ad valorem.
1883	41	Baryta, sulfate of, or barytes, manufactured	$\frac{1}{4}$ cent per pound.
1883	603	Baryta, carbonate of, or witherite	Free.
1890	49	Baryta, sulfate of, or barytes, including barytes earth:	
		Unmanufactured	$1.12 per ton.
		Manufactured	$6.72 per ton.
1890	500	Baryta, carbonate of, or witherite	Free.
1894	37	Baryta, sulfate of, or barytes, manufactured	$3 per ton.
1894	395	Baryta, carbonate of, or witherite, and baryta, sulfate of, or barytes, unmanufactured, including barytes earth	Free
1897	44	Baryta, sulfate of, or barytes, including barytes earth:	
		Unmanufactured	75 cents per ton.
		Manufactured	$5.25 per ton.
1897	489	Baryta, carbonate of, or witherite	Free.
1909	42	Baryta, sulfate of, or barytes, including barytes earth:	
		Unmanufactured	15 percent ad valorem.
		Manufactured	20 percent ad valorem.
1909	711	Witherite	Free.
1913	51	Baryta, sulfate of, or barytes, including barytes earth:	
		Unmanufactured	15 percent ad valorem.
		Manufactured	20 percent ad valorem.
1913	646	Witherite	Free
1922	69	Barytes ore, crude or unmanufactured	$4 per ton.
		Ground or otherwise manufactured	$7.50 per ton.

Duties levied on barite, manufactured and unmanufactured (meaning ground or crude), and provisions for witherite, Acts of 1883 to 1930. (Continued)

Act of –	Paragraph	Tariff classification	Rates of duty (all tons are 2,240 pounds)
1922	1698	Witherite..................................	Free.
1930	67	Barytes ore, crude........................	$4 per ton.
		Barytes ore, ground or manufactured....	$7.50 per ton.
1930	1801	Witherite, crude, unground..............	Free.

SPECIFICATIONS

The kind and amount of impurities permissible in barite depend on the use intended. In order of strictness of specification, the following uses and their requirements may be noted.

Glass. - Glassmakers who use barite as a furnace flux desire high purity, particularly with respect to iron oxide, small quantities of which tend to discolor glass. A typical analysis is $BaSO_4$, 98.0 percent; SiO_2, 1.5; Al_2O_3, 0.15; and Fe_2O_3, 0.15 percent. A typical mesh screen test is:

On	Percent
20	0
30	4.6
40	12.9
50	11.0
60	6.3
80	8.1
100	6.1
140	5.0
Through 140	46.0
	100.0

Barite of this analysis and screen size is not absolutely necessary. Indeed, glassmakers had to content themselves with material containing iron up to 0.5 percent Fe_2O_3 until competition induced producers to install magnetic separators. Also, during the war, when regular glass-grade barite was in short supply, glassmakers turned to well-drilling barite, which contained but 92 percent barium sulfate and as much as 1 percent iron oxide, sometimes more. Furthermore, it was ground to 325 mesh. However, in normal times a glass barite is not competitive if it contains more than 0.2 percent iron oxide.

Barium chemicals and lithopone. - These are conveniently considered together, but in some respects barite for use in chemicals is subject to a stricter specification. Both the intended use of the barium chemical and the method used to convert barite to the chemical must be kept in mind. During the war, a great deal of barium nitrate and peroxide has been used in green signal flares. As strontium gives a counteracting red color, manufacturers of these chemicals specified a typical strontium maximum of 1 percent. Lithopone makers do not specify any maximum of strontium sulfate; in any event, it could not possibly exceed 6 percent, assuming a 94 percent minimum of barium sulfate, and is ordinarily much lower. For both chemical and lithopone manufacture, barite analyzing 94 percent minimum barium sulfate is almost universally required. Ba present as barium carbonate is considered a diluent, as most of it is still present as barium carbonate after conversion of barite to black ash, and as such cannot be leached from the ash. Therefore, only Ba occurring as barium sulfate is included in the 94 percent barium sulfate minimum. Owing to its severe fluxing action in the black ash kiln, fluorine must be rigidly excluded. Only traces are permissible. This leaves iron, alumina, silica, and lime as the remaining impurities most commonly encountered. These impurities are not merely diluents; some of them inhibit the reduction of barite to the sulfide. Thus, it would be poor economy to pay 10 percent less for a 90 percent ore than for a 95 percent ore, as the additional 5 percent of impurities in the 90 percent ore would disproportionately reduce conversion of the barite to black ash. For example, Wuetrich[146] has found that iron reacts as follows: $BaSO_4 + Fe_2O_3 \rightarrow Ba(FeO_2)_2$ insoluble $+ SO_3$. Iron oxide also catalyzes the reaction: $BaSO_4 + SiO_2 \rightarrow BaO.SiO_2 + SO_3$. Monobarium silicate is also insoluble in water, and hence barium tied up in this way is not available when black ash is leached. It is important to note that silica is but slightly reactive if the iron content is low. Thus, in a barite containing 2 percent SiO_2 and only 0.07 percent Fe_2O_3, conversion to BaS in a laboratory furnace was 97.6 percent complete. But when Fe_2O_3 was raised to 1.46 percent (SiO_2 remaining at 2 percent), conversion dropped to 90.4 percent, indicating that besides reacting with BaO, the iron oxide had also catalyzed the reaction of barite with silica and other impurities.[146] In the same patent, Wuetrich pointed out the deleterious effect of calcium (which most often occurs in barite as calcite, dolomite, or gypsum). For example, barite containing 0.1 percent $CaSO_4$ gave a 94 percent conversion of $BaSO_4$ to BaS, whereas a similar barite, differing only in that the $CaSO_4$ content had been raised to 0.7 percent $CaSO_4$, reduced conversion to 90 percent. One manufacturer of barium chemicals specifies a CaO maximum of 0.1 percent; however, most specifications are silent on this point.

It has been reported[147] that Al_2O_3 inhibits conversion of $BaSO_4$, but actual restrictions of Al_2O_3 in specifications are rare, probably because there is seldom enough of it to be harmful.

Some lithopone makers specify that lead and other heavy metals be limited to traces, as most of the heavy metal sulfides are colored. This restriction is probably not necessary, as the heavy metals are precipitated as sulfides when the black ash is leached and therefore would not get into the lithopone.

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[146] Wuetrich, A. G., Treatment of Barytes: U. S. Patent 2,163,388, June 20, 1939.

[147] Hirschel, W., Die Fabrikation von Schwefelbarium: Chemiker-Zeitung, vol. 50, No. 88, Sept. 15, 1926, pp. 692-3.

In view of the fact that virtually all black ash is made in a rotary kiln, the reacting material must not be crushed too fine or dust will be lost. The regular jigged material available from washers in the East is crushed at the consuming plant to 4 to 20 mesh before use in the kiln. Ground material, such as that from Arkansas, could hardly be used as a kiln feed without pelletization. A wide field is open here for research. Against the disadvantage of the initial higher cost of ground barite, to which must be added the cost of pelletication, may be set the advantage of more intimate mixing with the powdered carbonaceous reducing material, with a consequent greater degree of reduction.

A typical specification of barite for lithopone and chemical use is 94 percent minimum $BaSO_4$, 1 percent Fe_2O_3 maximum, and F trace maximum. As previously pointed out, individual purchasers may add miscellaneous minor restrictions. Some purchasers buy on a premium-penalty basis, giving 25 cents a ton more for each additional percent of $BaSO_4$ over 94, with similar deductions below 94 percent, and 25 cents a ton more for each 0.1 percent Fe_2O_3 less than 1 percent, with similar deductions for Fe_2O_3 in excess of 1 percent. All analyses are on oven-dried samples. It is desired that jigged material be drained as thoroughly as possible so that the buyer will not have to pay freight on the moisture content; also the ore freezes into solid masses in bins and stock piles if it is wet.

Well drilling. - The main requisite of a mud-weighting material is that it be heavy and inert. Barite meets these requirements admirably, even when it is somewhat impure. Thus, a material containing only 92 percent $BaSO_4$ and as much as 2 or 3 percent iron oxide would be unsuitable for lithopone but excellent for well drilling. Grinders of barite for the well-drilling trade try to maintain a $BaSO_4$ content of 92 percent, or, failing that, a specific gravity of 4.2; the latter is the more important. Nearly all prewar "mud weight" had a specific gravity of 4.2 or better, but this was largely a matter of competition, for during the war shortage, material of only 4.0, sometimes even less, has been gladly accepted by drilling contractors. There must be no soluble salts in the barite. Calcium sulfate is included in this description, although only slightly soluble, because small quantities suffice to flocculate bentonite. A specification is quite common among well drillers in the Gulf area which limits insoluble carbonates (such as $CaCO_3$ and $BaCO_3$) to 0.1 percent maximum. This odd restriction came into being because insoluble carbonates in Missouri barite were virtually absent when barite was first used for weighting drilling muds, and the major purchasers have adhered to the specification of the barite first used by them because it has been found satisfactory. To this specification should be contrasted the analysis of barite shipped from El Portal, Calif., which may carry 10 or 15 percent $BaCO_3$, and is said to be perfectly satisfactory even in the deepest wells.

Fillers. - There are two typical grades of barite used in fillers. One is a grade corresponding substantially to that used in making chemicals and lithopone; it is ground and bleached. The other is "off-color", the only requirement being that it be fairly heavy and not be too dark in color. Impurities are largely immaterial in the latter substance except as they contribute to too much discoloring. Barite for off-color fillers has been known to analyze as low as 62 percent $BaSO_4$, but discoloring constituents,

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such as iron oxide, were less than 0.2 percent. Most of the impurities were silica and fluorite.

WITHERITE

Description

Witherite is native barium carbonate. The pure mineral analyses 77.7 percent BaO and 22.3 percent CO_2, as against 65.7 percent BaO in barite. Its hardness is between 3 and 4 on Mohs' scale, and its specific gravity is approximately 4.3, compared with 4.5 for barite.

Occurrences

Known occurrences of witherite in the United States have been summarized by Johnson.[148] Johnson's findings and references are repeated below:

> In the United States, witherite deposits occur in Alaska, Arizona, California, Kentucky, Montana, Nevada, New Mexico, and Tennessee. The deposits in Kentucky, Nevada, and Tennessee appear to be small and of mineralogic interest only. In Kentucky crystals of witherite have been found in some of the fluorspar-galena veins in the central part of the State.[149] In Nevada only occasional small crystals of witherite have been found. These were in barite veins near Argenta, Lander County.[150] In Tennessee a small quantity of witherite is reported as a surface alteration product in a barite vein in Rutherford County.[151] No details are available regarding the New Mexican occurrences reported in Socorro and Dona Ana Counties.[152] The deposits in Alaska, Arizona, and Montana contain considerable witherite, but the extent of each of these deposits is still unknown. According to correspondence from the Alaska Department of Mines dated November 24, 1941, and February 17, 1942, the Alaska deposits on the shore of Kuiu Island, in southeastern Alaska, consist of a short irregular vein averaging 16 inches thick, scattered small veinlets, and beach pebbles.

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[148] Johnson, B. L., and Warner, K. G., Bureau of Mines Minerals Yearbook 1941, pp. 1446-1447.

[149] Jillson, W. R., The Geology and Mineral Resources of Kentucky: Kentucky Geol. Survey, 1928, 409 pp. (See p. 103.)
Robinson, L. C., Vein Deposits of Central Kentucky: Kentucky Geol. Survey, ser. 6, vol. 41, 1931. (See pp. 28, 48, 118.)

[150] Gianella, V. P., Barite Deposits of Northern Nevada: Am. Inst. Min. and Met. Eng., Tech. Pub. 1200, 1940, 6 pp.

[151] Jewell, W. B., Barite, Fluorite, Galena, Sphalerite Veins in Central Tennessee: Paper presented at the Tuscaloosa (Ala.) meeting of the Industrial Minerals Division, Am. Inst. Min. and Met. Eng., November 3, 1939.

[152] Jones, F. A., The Mineral Resources of New Mexico: State School of Mines, Mineral Resources Survey of New Mexico, Bull. 1, Socorro, N. Mex., 1915, 77 pp.

comprising in all a very small tonnage. In Arizona, witherite forms about 5 percent of the gangue of certain lead veins in the Castle Dome district, Yuma County, according to a letter from F. W. Galbraith of the Arizona Bureau of Mines dated January 20, 1942.[153] The Montana deposits consist of lenses and masses of witherite and irregular lumps up to 2 feet in diameter in solution cavities in Altyn pre-Cambrian limestone just above the plane of the Lewis overthrust fault at Many Glacier in Glacier National Park.[154]

Witherite occurs in California in Mariposa and Shasta Counties. In Mariposa County it is associated with barite in veins, cutting sedimentary rocks on the western flank of the Sierra Nevada granite batholith in two localities about 6 miles apart. The northernmost of these, in the Merced River Valley near the El Portal entrance of Yosemite National Park, consists of a group of steeply dipping veins striking north. The veins apparently were formed by replacement of limestone in an isoclinally folded series of Carboniferous sediments by barium-bearing solutions given off by the underlying Jurassic (or Cretaceous) Sierra Nevada granite batholith. This group of veins,[155] reported traceable over a distance of 3 miles, provides a mixture of witherite and barite sold as a flux to glassmakers. [It is no longer sold for this use.] The other locality in Mariposa County is at Devil's Gulch, 6 miles south of El Portal, where a north-striking replacement deposit of barite and witherite in limestone is reported traceable 4,500 feet.[156] In Shasta County massive witherite is reported on Beegum Creek near Platina.[157]

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[153] Johnson, B. L., Witherite - Arizona: Bureau of Mines Mineral Trade Notes, vol. 14, No. 2, February 20, 1942, p. 27.

[154] Fuller, M. P., An Occurrence of Witherite in the Altyn Limestone at Many Glacier, Mont.: Am. Mineral., vol. 9, No. 7, July 1924, p. 154.

[155] Fitch, A. A., Barite and Witherite from near El Portal, Mariposa County, Calif.: Am. Mineral., vol. 16, 1931, pp. 461-468.
Bradley, W. W., Witherite in the Americas: Eng. and Min. Journ., vol. 132, No. 12, Dec. 28, 1931, p. 538. Barite in California: Trans. Am. Inst. Min. and Met. Eng., 1931, pp. 170-176.
Julihn, C. E., and Horton, F. W., Mineral Industries Survey of the United States; California. Mines of the Southern Mother Lode Region. Part II, Tuolumne and Mariposa Counties: Bureau of Mines Bull. 424, 1940, 179 pp.
Harding, A. C., Ground Barytes for Weighting Drilling Mud: Eng. and Min. Jour., vol. 142, No. 1, January 1941, pp. 33-36.

[156] Julihn, C. E., and Horton, F. W., Work cited in footnote 155.

[157] Bradley, W. W., Work cited in footnote 155.

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Uses

Although witherite is not mined separately in the United States, some is mined intermixed with barite at El Portal, Calif., and sold for weighting oil-well drilling muds without separation. The world's sole commercial source of witherite is northern England, and in that country it is the principal barium raw material. Witherite is imported into the United States for use in scum-prevention in ceramics, in case-hardening steel, and as "make-up" carbonate in the conversion of precipitated barium carbonate to barium hydroxide for use in sugar purification (in Colorado). For uses not requiring a very fine particle size or a purity greater than 90 to 92 percent $BaCO_3$ (standard witherite analysis), witherite is probably as usable as precipitated $BaCO_3$.

Barium salts are obtained from witherite by reaction with the proper acid. The hydroxide is generally obtained by the Deguide process,[158] in which barium carbonate is calcined with monobarium silicate in a rotary kiln at 1,400° to 1,500° C., when the following reaction occurs: $BaO.SiO_2 + 2BaCO_3 \rightarrow SiO_2.3BaO + 2CO_2$. The tribarium silicate thus obtained is hydrolyzed: $SiO_2.3BaO + 2H_2O \rightarrow 2Ba(OH)_2 + SiO_2.BaO$. Both the monobarium silicate and the barium carbonate are cyclic, the silicate being regenerated in the process just outlined and the carbonate recovered in the sugar process as explained on p. 41. Make-up of the silicate is provided by the addition of silicate to the kiln batch and of the carbonate by addition of witherite or manufactured barium carbonate to the batch.

It has been recommended[159] that 2 to 5 percent of ground witherite be added to portland cement to retard the leaching of lime from underwater concrete, but such use is questionable, as there is very little free lime in good concrete.

Witherite is used to some extent as a paint filler in England, but little or none is used for this purpose in the United States.

A good general reference on witherite is given in the footnote.[160]

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[158] Deguide, C., Process for Obtaining Barium Hydrate: U. S. Patent 1,247,510, Nov. 20, 1917.

[159] Settlingstones Mines, Ltd., Work cited in footnote 108 on pp. 38-40.

[160] Meyer, H. C., Occurrences and Uses of Witherite: Foote-Prints, vol. 5, No. 1, May 1942, pp. 3-19.

STATISTICAL APPENDIX[161]

Since about 1900, with the exception of the two war periods, Germany has been the leading producer of barite in the world, furnishing about half the output. Most of the German production was from the area of Meggen-on-Lenne, Westphalia, Prussia, in a bedded deposit. This material, discolored by bituminous matter, was used in nearby lithopone and chemical plants and also exported to consumers on the Atlantic seaboard of the United States. There has also been substantial production from vein deposits in Germany. In 1943 and 1944 a cut near Walton, Nova Scotia, yielded considerable barite, much of which was imported duty free into the United States to relieve the shortage in the East.

An excellent reference on foreign barite deposits and foreign trade data is given in the footnote [162].

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[161] Figures on imports and exports compiled from records of the Department of Commerce.

[162] Simpson, J., Barium Minerals: 2d ed., Imperial Institute (London), 1937, 84 pp.

World production of barite, 1908-44, by countries, in metric tons[1]

Country	1908	1909	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920	1921	1922	1923	1924	1925	1926
Algeria	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	1,200	700	500	600	800
Australia	(2)	(2)	(2)	(2)	(2)	550	739	374	1,244	1,275	2,069	2,827	3,874	1,494	1,927	1,891	2,080	2,247	1,973
Austria	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	2,080	2,140	2,377	1,399	1,363	966
Belgium	25,070	31,399	4,900	25,200	32,400	12,000	(2)	(2)	(2)	(2)	(2)	—	15,240	17,050	1,480	6,770	20,490	13,190	6,100
Canada	3,912	162	—	45	421	582	555	499	1,241	3,166	581	425	681	245	262	371	137	86	91
France	16,277	14,111	11,632	10,064	13,619	12,236	(2)	(2)	(2)	(2)	(2)	11,861	18,782	11,297	12,634	26,061	44,189	41,450	38,810
Germany:																			
Baden	(2)	(2)	(2)	(2)	(2)	16,441	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
Bavaria	17,195	17,920	24,711	26,234	27,198	27,192	18,013	7,143	12,484	10,199	5,507	8,804	7,888	23,439	16,139	19,970	23,029	21,477	26,955
Prussia	(2)	(2)	(2)	(2)	(2)	34,627	26,070	14,273	18,580	17,472	22,454	54,384	103,976	85,322	164,365	97,207	102,326	151,243	135,319
Saxony	(2)	(2)	(2)	(2)	(2)	134	64	—	—	—	—	—	—	—	—	—	2,076	968	—
Unspecified	8,554	15,186	13,832	15,014	15,871	—	—	—	—	—	—	—	—	—	—	—	—	—	—
India (British)	(2)	(2)	(2)	(2)	(2)	—	(2)	(2)	(2)	(2)	2,768	2,632	689	1,718	2,430	2,611	2,340	1,473	2,348
Italy	15,731	16,239	14,420	13,619	13,420	12,970	12,970	17,850	21,650	19,000	12,300	15,920	15,380	13,500	21,300	27,592	39,568	32,195	31,845
Japan	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	48	47	—	—	—
Southern Rhodesia	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	49	—	—	—	—	9	64	36	27
Spain	334	422	476	635	1,096	3,049	2,474	4,218	10,508	10,147	4,170	11,459	13,773	9,650	7,705	18,434	14,450	8,784	7,941
U.S.S.R. (Russia)[3]	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	328	(2)	1,000	60	737	4,684	14,389
United Kingdom (Great Britain)	39,572	42,436	45,383	44,826	46,105	50,848	49,715	63,480	77,254	66,609	67,425	61,051	65,180	25,065	41,606	44,195	55,646	49,462	43,462
United States	34,951	56,195	38,986	35,125	32,244	42,129	46,204	97,589	205,217	197,430	138,107	193,410	201,551	87,350	120,936	192,552	182,567	213,654	215,205

Country[4]	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944
Algeria	500	—	1,200	2,403	944	890	10	—	—	—	2,137	3,069	(2)	(2)	2,580	2,753	2,988	1,340
Argentina	—	—	—	—	—	—	—	—	—	—	—	—	768	2,680	4,174	7,083	(2)	(2)
Australia	2,119	2,424	2,167	1,736	1,592	2,037	2,128	2,532	2,585	2,192	3,152	3,231	4,216	5,047	4,990	6,512	(2)	(2)
Austria	1,924	2,243	300	496	87	275	1,030	1,025	797	1,663	855	373	(2)	(2)	(2)	(2)	(2)	(2)
Belgium	1,630	740	—	—	—	—	—	—	—	—	—	—	—	(2)	(2)	(2)	(2)	(2)
Brazil	—	—	—	—	—	1,229	891	(2)	(2)	(2)	5/500	600	(2)	(2)	(2)	(2)	(2)	(2)
Canada	51	115	95	60	15	—	18	—	(2)	(2)	—	—	(2)	307	6,250	17,842	22,202	103,770
China	(2)	(2)	(2)	(2)	(2)	505	3,092	9,500	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
Chosen	(2)	(2)	(2)	6,096	5,460	6,569	4,969	5,935	11,027	5,113	8,400	(2)	(2)	(2)	(2)	(2)	(2)	(2)
Cuba (exports)	—	—	—	—	—	—	—	—	—	—	3,659	6,163	10,671	16,105	13,223	3,787	3,158	4,787
Czechoslovakia	(2)	(2)	(2)	(2)	(2)	(2)	(2)	2,094	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
Egypt	—	—	—	—	—	—	—	50	85	30	51	20	31	61	30	60	76	19
France	28,300	30,050	41,625	32,650	11,300	10,400	13,700	18,350	16,900	22,200	19,850	(2)	(2)	2,246	4,494	9,563	5,589	2,513
Germany:																		
Baden	(2)	(2)	(2)	(2)	(2)	(2)	(2)	19,681	12,445	17,800	21,653	36,305	(2)	(2)	(2)	(2)	(2)	(2)
Bavaria	20,035	23,872	23,406	17,778	7,835	5,853	4,146	8,385	7,073	11,175	11,532	26,748	(2)	(2)	(2)	(2)	(2)	(2)
Prussia[6]	154,794	232,858	260,811	217,925	160,482	102,167	143,465	326,318	326,950	392,103	410,634	401,906	(2)	(2)	(2)	(2)	(2)	(2)
Saxony	—	1,401	1,870	430	2,534	2,446	130	484	222	467	432	230	(2)	(2)	(2)	(2)	(2)	(2)
Thuringia	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	554	450	6,700	15,315	(2)	(2)	(2)	(2)	(2)	(2)
Württemburg	(2)	(2)	(2)	(2)	(2)	—	(2)	(2)	(2)	1,000	192	—	(2)	(2)	(2)	(2)	(2)	(2)
Greece	—	—	—	—	—	—	—	7,853	23,091	31,336	39,343	34,700	24,055	(2)	(2)	(2)	(2)	(2)
India (British)	1,747	3,146	3,810	6,906	5,745	3,004	5,742	3,874	5,581	5,196	15,941	8,205	9,404	19,079	23,844	11,462	9,002	(2)
Indochina	—	—	—	—	—	—	—	—	—	40	45	50	155	185	(2)	(2)	(2)	(2)
Irish Free State (Eire)	(2)	—	41	1,524	864	—	—	—	—	—	(2)	(2)	(2)	(2)	(2)	(2)	5,485	(2)
Italy	30,677	27,116	25,955	19,319	24,326	21,861	23,444	32,408	41,152	36,671	45,202	48,169	53,893	(2)	(2)	(2)	(2)	(2)
Japan	(2)	(2)	(2)	(2)	(2)	(2)	—	—	—	3,837	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
Norway	—	—	—	—	—	—	—	—	—	408	70	—	—	(2)	(2)	(2)	(2)	(2)
Portugal	—	—	—	—	80	—	2	1	—	10	113	24	25	20	46	(2)	1	(2)
Southern Rhodesia	13	77	264	249	—	—	—	14	—	—	—	91	50	(2)	(2)	(2)	(2)	(2)
Spain	7,716	6,163	5,806	5,552	8,539	8,934	4,605	17,528	19,077	—	—	500	8,856	9,936	8,125	7,801	6,309	7,490
Switzerland	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	256	268	253
Union of South Africa	(2)	(2)	(2)	(2)	(2)	(2)	(2)	1,732	627	583	570	491	439	691	1,390	745	2,740	(2)
U.S.S.R. (Russia)	3/8,496	3/3,937	3/11,100	24,300	43,100	24,300	31,000	74,800	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
United Kingdom	47,605	50,702	58,011	59,647	46,312	57,548	67,689	75,182	79,366	74,242	74,485	77,543	7/96,333	7/126,331	7/103,167	7/100,312	7/102,736	(2)
United States	194,313	235,650	250,332	215,460	191,351	121,174	132,813	161,806	197,833	248,624	327,380	304,298	331,910	354,219	438,523	408,116	389,451	467,321

[1] Source: Inf. Circ. 6221, Barite and Barium Products, Part 1; Mineral Resources of the United States; and Minerals Yearbook. [2] Data not available. [3] Year ended Sept. 30. [4] The following countries did not produce in the years 1908-26 so far as is known: Argentina, Brazil, China, Chosen, Cuba, Czechoslovakia, Egypt, Greece, Indochina, Irish Free State, Norway, Portugal, Switzerland, and Union of South Africa. [5] Exports.
[6] 1929-38: Official figures which, it is reported, cover only output of mines included under the mining law. Also probably applies to earlier years, although the foreign source of information is not clear on this point.
[7] Includes witherite.

Primary barite in the United States, 1900-44

Year	Domestic production, short tons	Imports: Crude, Short tons	Imports: Crude, Foreign value	Imports: Ground, Short tons	Imports: Ground, Foreign value	Apparent new supply, short tons
1900	67,680	2,568	$8,301	2,454	$24,160	72,702
1901	49,070	3,150	12,380	2,454	27,062	54,674
1902	61,668	3,929	14,322	3,908	37,389	69,505
1903	50,397	7,105	22,777	5,716	48,726	63,218
1904	65,727	7,492	27,363	6,630	48,658	79,849
1905	48,235	14,256	62,459	4,803	39,803	67,294
1906	50,231	9,190	27,584	4,807	37,296	64,228
1907	89,621	20,544	76,883	11,207	96,542	121,372
1908	38,527	13,661	58,822	3,401	29,168	55,589
1909	61,945	11,647	29,028	3,016	25,679	76,608
1910	42,975	21,270	48,457	3,565	29,782	67,810
1911	38,719	20,214	36,643	3,147	22,083	62,080
1912	35,543	26,186	52,467	3,679	26,848	65,408
1913	46,440	35,840	61,409	5,463	38,155	87,743
1914	51,593	24,423	46,782	4,323	30,483	80,339
1915	107,574	2,504	4,877	1,308	10,736	111,386
1916	226,214	17	245	147	2,072	226,378
1917	217,630	6	63	88	1,743	217,724
1918	152,238	-	-	-	-	152,238
1919	213,199	118	594	-	-	213,317
1920	222,173	24,874	146,858	274	3,017	247,321
1921	96,287	11,054	59,371	1,002	16,942	108,343
1922	133,310	23,239	104,680	4,696	59,453	161,245
1923	212,253	15,045	93,721	6,022	88,741	233,320
1924	201,247	21,502	104,264	2,830	38,292	225,579
1925	235,515	28,655	91,016	3,203	40,008	267,373
1926	237,224	51,016	195,004	3,347	44,781	291,587
1927	214,194	70,274	253,284	3,259	38,568	287,727
1928	259,761	61,765	190,756	3,098	33,378	324,624
1929	275,945	85,729	284,436	2,924	34,619	364,598
1930	237,505	52,111	179,579	2,331	26,905	291,947
1931	210,930	73,080	329,114	1,851	22,415	285,861
1932	133,572	45,758	177,954	1,594	16,757	180,924
1933	146,402	49,958	216,955	2,632	30,492	198,992
1934	178,361	40,031	174,937	1,863	16,916	220,255
1935	218,075	47,048	246,254	3,354	28,766	268,477
1936	274,062	33,843	170,316	2,873	28,397	310,778
1937	360,877	64,992	327,224	3,313	35,046	429,182
1938	335,433	24,845	151,235	1,700	15,466	361,978
1939	365,870	11,588	55,985	1,590	14,999	379,048
1940	390,462	7,391	41,342	314	3,299	398,167
1941	483,391	456	2,518	-	-	483,847
1942	449,873	4,680	34,756	-	-	454,553
1943	429,298	-	-	-	-	429,298
1944	515,136	67,888	459,664	11,964	243,917	594,988

Crude barite sold or used by producers in the United States, 1901-44, by States [1]

Year	Alabama		Arizona		California		Georgia		Kentucky		Missouri		Nevada		North Carolina		Tennessee		Virginia		Other States [2]		Totals	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
1901....	—	—	—	—	—	—	(3)	(3)	—	—	20,750	$73,714	—	—	[3] 7,390	[3] $22,615	10,460	$30,155	10,270	$31,260	—	—	49,070	$157,844
1902....	—	—	—	—	—	—	—	—	—	—	31,734	104,677	—	—	14,679	44,130	2,855	14,647	12,400	39,700	—	—	61,668	203,154
1903....	—	—	—	—	—	—	—	—	(4)	(4)	23,773	77,712	—	—	6,335	21,347	[4] 14,594	[4] 32,691	5,700	20,400	—	—	50,397	152,150
1904....	—	—	—	—	—	—	—	—	(4)	(4)	25,494	76,152	—	—	13,417	33,330	[4] 15,602	[4] 34,024	11,214	31,452	—	—	65,727	174,958
1905....	—	—	—	—	—	—	—	—	(4)	(4)	26,801	84,295	—	—	5,519	21,545	[4] 9,447	[4] 15,325	6,468	27,433	—	—	48,235	148,203
1906....	(5)	(5)	—	—	—	—	—	—	(5)	(5)	28,869	93,479	—	—	(5)	(5)	5,247	8,782	11,775	45,336	4,340	$12,770	50,231	160,367
1907....	—	—	—	—	—	—	(5)	(5)	(5)	(5)	44,339	162,459	—	—	5,785	18,855	20,561	37,138	9,254	32,833	9,682	40,492	89,621	291,777
1908....	—	—	—	—	—	—	(5)	(5)	5,233	$21,504	16,719	54,768	—	—	(5)	(5)	8,618	12,313	(5)	(5)	8,357	31,857	38,927	120,442
1909....	—	—	—	—	—	—	(5)	(5)	(4)	(4)	34,815	119,818	—	—	(5)	(5)	[4] 15,606	[4] 55,867	(5)	(5)	11,524	34,052	61,945	209,737
1910....	—	—	—	—	—	—	(5)	(5)	(4)	(4)	22,668	75,598	—	—	(5)	(5)	[4] 6,903	[4] 13,348	(5)	(5)	13,404	32,800	42,975	121,746
1911....	—	—	—	—	—	—	(5)	(5)	(4)	(4)	21,600	81,380	—	—	(5)	(5)	[4] 8,719	[4] 20,053	(5)	(5)	8,126	21,359	38,445	122,792
1912....	—	—	—	—	—	—	(5)	(5)	—	—	24,530	117,035	—	—	(5)	(5)	3,718	8,682	(5)	(5)	9,230	27,596	37,478	153,313
1913....	—	—	—	—	—	—	(5)	(5)	—	—	31,131	117,638	—	—	(5)	(5)	2,098	3,568	(5)	(5)	12,069	35,069	45,298	156,275
1914....	(5)	(5)	—	—	(5)	(5)	(5)	(5)	(5)	(5)	33,317	112,251	—	—	(5)	(5)	10,113	16,273	(5)	(5)	9,317	27,143	52,747	155,667
1915....	(5)	(5)	—	—	(5)	(5)	31,027	$100,825	7,753	27,427	40,113	131,597	—	—	(5)	(5)	25,074	71,390	(5)	(5)	5,580	19,793	109,547	351,032
1916....	7,631	$27,198	—	—	(5)	(5)	104,754	401,295	11,068	54,995	58,223	365,111	(5)	(5)	878	3,246	32,416	123,986	(5)	(5)	6,952	35,401	221,952	1,011,232
1917....	1,976	8,868	—	—	(5)	(5)	111,300	601,895	6,720	36,084	59,046	391,363	(5)	(5)	1,013	5,080	16,272	79,053	(5)	(5)	9,455	48,136	206,228	1,171,184
1918....	1,794	9,976	—	—	—	—	69,318	413,173	(5)	(5)	46,004	393,723	(5)	(5)	(5)	(5)	22,542	141,944	(5)	(5)	12,600	81,169	152,368	1,044,905
1919....	(5)	(5)	—	—	(5)	(5)	85,303	667,521	5,435	36,408	73,247	640,398	(5)	(5)	(5)	(5)	34,700	288,622	(5)	(5)	10,645	94,873	209,330	1,727,822
1920....	(5)	(5)	—	—	2,250	$20,350	84,644	790,362	(5)	(5)	99,954	1,014,070	(5)	(5)	(5)	(5)	29,319	213,657	(5)	(5)	12,246	104,025	228,413	2,142,464
1921....	(5)	(5)	—	—	942	5,354	24,624	191,442	—	—	25,220	217,913	—	—	(5)	(5)	8,150	61,148	(5)	(5)	7,433	56,171	66,369	531,958
1922....	(5)	(5)	—	—	3,335	17,707	57,045	463,517	—	—	66,421	421,568	—	—	(5)	(5)	16,642	124,204	—	—	11,594	91,094	155,040	1,118,950
1923....	(5)	(5)	—	—	(5)	(5)	83,291	670,343	(5)	(5)	81,701	635,097	—	—	1,179	7,076	34,994	253,005	(5)	(5)	13,028	98,635	214,193	1,664,156
1924....	(5)	(5)	—	—	—	—	71,776	574,208	—	—	77,189	604,790	(5)	(5)	(5)	(5)	39,643	302,473	(5)	(5)	7,724	59,273	196,332	1,540,744
1925....	—	—	(5)	(5)	—	—	65,236	475,618	—	—	101,056	794,927	(5)	(5)	(5)	(5)	47,012	345,038	(5)	(5)	14,059	87,514	227,363	1,703,097
1926....	—	—	(5)	(5)	(5)	(5)	77,654	532,706	(5)	(5)	117,919	946,595	(5)	(5)	—	—	20,910	155,780	(5)	(5)	20,392	138,212	236,875	1,773,293
1927....	—	—	—	—	13,919	71,708	94,039	580,300	—	—	111,456	797,455	884	$3,969	—	—	20,537	129,999	(5)	(5)	13,430	87,437	254,265	1,670,878
1928....	—	—	—	—	12,557	51,502	112,316	675,509	—	—	114,274	810,203	—	—	—	—	20,260	150,937	(5)	(5)	10,137	66,773	269,544	1,754,924
1929....	—	—	—	—	24,701	147,762	94,115	546,212	—	—	119,679	880,719	618	6,384	—	—	26,140	181,725	(5)	(5)	12,813	88,304	277,269	1,850,706
1930....	—	—	—	—	19,517	114,310	41,746	238,769	—	—	132,640	938,812	2,647	19,457	—	—	17,006	111,981	10,250	73,168	11,176	49,674	234,982	1,546,171
1931....	—	—	2,139	$14,275	17,500	102,085	(5)	(5)	—	—	93,417	539,152	1,400	9,600	—	—	10,170	62,903	(5)	(5)	49,894	266,640	174,520	994,655
1932....	—	—	1,271	6,896	7,789	55,746	(5)	(5)	—	—	85,458	463,347	(5)	(5)	100	465	2,825	15,702	(5)	(5)	32,411	202,199	129,854	744,355
1933....	—	—	—	—	9,266	54,404	(5)	(5)	—	—	112,335	510,551	(5)	(5)	—	—	(5)	(5)	(5)	(5)	46,279	287,656	167,880	852,611
1934....	—	—	—	—	21,783	124,664	(5)	(5)	—	—	118,836	581,889	(5)	(5)	—	—	(5)	(5)	(5)	(5)	69,231	402,825	209,850	1,109,378
1935....	—	—	—	—	(5)	(5)	30,577	178,254	—	—	131,921	727,888	(5)	(5)	—	—	(5)	(5)	(5)	(5)	62,613	345,126	225,111	1,251,268
1936....	—	—	—	—	(5)	(5)	34,435	206,336	—	—	160,866	1,008,528	(5)	(5)	—	—	(5)	(5)	(5)	(5)	85,859	459,767	281,160	1,674,631
1937....	—	—	—	—	(5)	(5)	71,044	405,677	—	—	198,101	1,430,597	(5)	(5)	—	—	(5)	(5)	(5)	(5)	85,843	404,696	354,988	2,240,970
1938....	—	—	(5)	(5)	(5)	(5)	64,304	317,329	—	—	156,539	1,150,630	(5)	(5)	—	—	29,398	206,040	—	—	53,422	330,522	303,663	2,004,521
1939....	(5)	(5)	(5)	(5)	(5)	(5)	86,589	474,378	—	—	172,642	1,167,870	(5)	(5)	—	—	57,140	372,348	(5)	(5)	69,238	329,507	385,609	2,344,103
1940....	—	—	—	—	(5)	(5)	92,302	464,290	—	—	179,455	1,216,369	(5)	(5)	—	—	70,767	503,204	(5)	(5)	66,829	412,880	409,353	2,596,743
1941....	—	—	—	—	(5)	(5)	104,446	583,445	—	—	212,718	1,337,756	(5)	(5)	—	—	104,511	779,565	(5)	(5)	81,481	467,469	503,156	3,134,234
1942....	(5)	(5)	—	—	(5)	(5)	86,676	487,261	—	—	146,270	943,131	(5)	(5)	—	—	83,291	624,584	(5)	(5)	113,247	622,026	429,484	2,677,002
1943....	—	—	(5)	(5)	(5)	(5)	98,620	621,193	(5)	(5)	124,147	872,044	12,157	49,900	—	—	52,593	383,007	—	—	172,766	870,632	460,283	2,796,776
1944....	—	—	—	—	(5)	(5)	107,251	929,090	—	—	150,748	1,121,678	22,390	84,859	(5)	(5)	43,033	279,567	—	—	195,195	1,143,295	518,617	3,558,489

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[1] Source: 1901-31, Mineral Resources of the United States; 1932-44, Minerals Yearbook.

[2] 1906: Alabama, Kentucky, and North Carolina. 1907: Georgia and Kentucky. 1908-10: Georgia, North Carolina, and Virginia. 1911: Georgia, North Carolina, South Carolina, and Virginia. 1912: Georgia, North Carolina, and Virginia. 1913: Georgia, North Carolina, South Carolina, and Virginia. 1914: Alabama, California, Georgia, Kentucky, North Carolina, South Carolina, and Virginia. 1915: Alabama, Alaska, California, North Carolina, South Carolina, and Virginia. 1916: California, Colorado, Nevada, South Carolina, and Virginia. 1917: California, Nevada, South Carolina, and Virginia. 1918: Kentucky, Nevada, New Mexico, North Carolina, South Carolina, Virginia, and Wisconsin. 1919: Alabama, California, Illinois, Nevada, North Carolina, South Carolina, Virginia, and Wisconsin. 1920: Alabama, Illinois, Kentucky, Nevada, North Carolina, South Carolina, Virginia, and Wisconsin. 1921: Alabama, Illinois, North Carolina, South Carolina, and Virginia. 1922: Alabama, Idaho, Illinois, North Carolina, and South Carolina. 1923: Alabama, California, Kentucky, South Carolina, Virginia, and Wisconsin. 1924: Alabama, Nevada, North Carolina, South Carolina, Virginia, and Wisconsin. 1925: Arizona, Nevada, North Carolina, South Carolina, Virginia, and Wisconsin. 1926: Arizona, California, Illinois, Kentucky, Nevada, South Carolina, Virginia, and Wisconsin. 1927: South Carolina, Virginia, and Wisconsin. 1928: Colorado, South Carolina, Virginia, and Wisconsin. 1929: South Carolina, Virginia, and Wisconsin. 1930: South Carolina and Wisconsin. 1931: Georgia and Virginia. 1932: Georgia, Nevada, South Carolina, and Virginia. 1933-34: Georgia, Nevada, South Carolina, Tennessee, and Virginia. 1935: California, Nevada, South Carolina, Tennessee, and Virginia. 1936: California, Nevada, Tennessee, and Virgania. 1937: California, Nevada, Tennessee, Texas, and Virginia. 1938: Arizona, California, Nevada, South Carolina, and Texas. 1939: Alabama, Arizona, California, Colorado, Montana, Nevada, South Carolina, and Virginia. 1940-41: Arkansas, California, Colorado, Nevada, South Carolina, Texas, and Virginia. 1942: Alabama, Arkansas, California, Nevada, South Carolina, and Virginia. 1943: Arizona, Arkansas, California, Kentucky, and South Carolina. 1944: Arkansas, California, North Carolina, and South Carolina.

[3] Georgia included in North Carolina.

[4] Kentucky included in Tennessee.

[5] Included under "Other States."

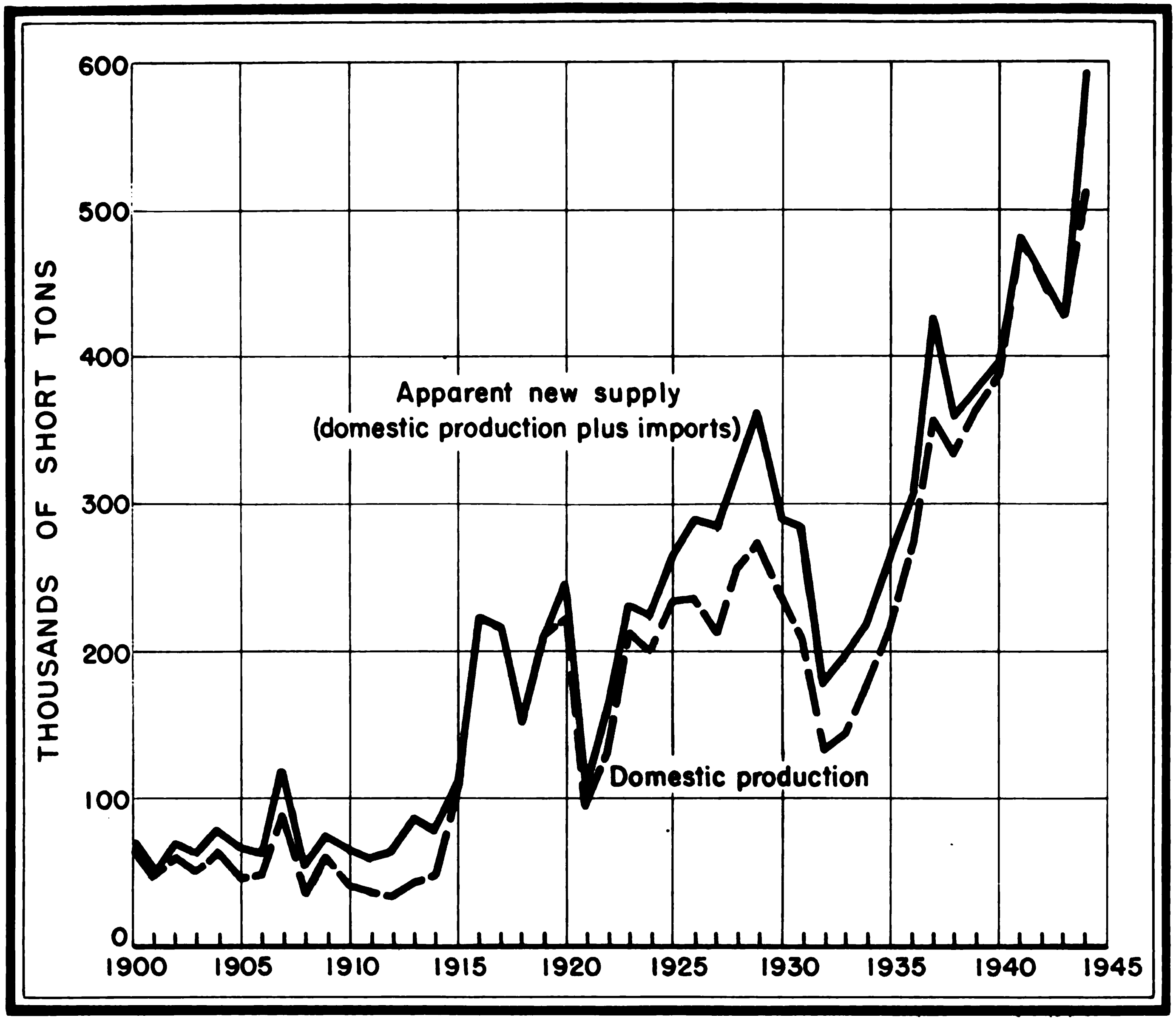

Figure 1. - Apparent new supply of barite in the United States, 1900-1944.

Ground (and crushed) barite sold or used by producers in the United States, 1908-44

Year	Plants	Short tons	Value	Average price
1908[1]	6	28,415	$318,096	$11.19
1909[1]	6	34,673	455,506	13.14
1910[1]	7	38,165	475,001	12.45
1911[1]	7	39,611	503,867	12.72
1912[1]	6	38,225	495,895	12.97
1913[1]	6	37,033	525,300	14.18
1914[1]	5	35,815	463,858	12.95
1915[1]	9	51,557	635,318	12.32
1916	9	65,440	964,802	14.74
1917	7	52,694	951,220	18.05
1918	9	55,086	1,041,608	18.91
1919	9	[2]57,985	1,163,437	20.06
1920	8	65,748	1,381,868	21.02
1921	7	27,661	622,871	22.52
1922	7	46,176	933,722	20.22
1923	6	39,605	895,095	22.60
1924	5	38,296	784,881	20.50
1925	5	49,674	1,040,461	20.95
1926	5	57,812	1,186,563	20.52
1927	7	57,658	1,166,294	20.23
1928	8	64,425	1,332,228	20.68
1929	8	54,472	914,516	16.79
1930	6	55,284	1,140,305	20.63
1931	9	32,297	656,769	20.34
1932	12	33,842	563,902	16.66
1933	13	34,601	683,432	19.75
1934	13	53,326	1,006,905	18.88
1935	11	76,250	1,407,787	18.46
1936	13	69,102	1,217,818	17.62
1937	12	129,777	2,249,612	17.33
1938	14	161,422	2,786,823	17.26
1939	13	170,695	2,902,973	17.01
1940	16	184,390	3,697,806	20.05
1941	16	234,877	4,606,832	19.61
1942	19	178,765	3,611,745	20.20
1943	18	208,252	3,743,919	17.98
1944	19	344,757	5,455,835	15.83

[1] Sales of refined barite (domestic only).

[2] Figures cover production, not sales.

Ground (and crushed) barite sold or used by producers, 1938-44, by consuming industries, in short tons

Year	Well drilling	Paint	Glass	Rubber	Undistributed	Total
1938......	126,697	8,227	7,963	2,944	15,591	161,422
1939......	125,560	9,750	12,586	3,319	19,480	170,695
1940......	138,055	11,056	12,697	4,283	18,299	184,390
1941......	154,760	31,009	22,615	9,800	16,693	234,877
1942......	117,380	18,484	21,895	6,334	14,672	178,765
1943......	144,452	15,000	25,464	8,000	15,336	208,252
1944......	277,792	23,000	24,153	10,000	9,812	344,757

Until lithopone was invented, virtually all barite was ground for use as filler. However, increasing quantities were consumed for lithopone, and by the end of World War I barite was used mainly for lithopone, about two thirds of the output having been consumed thus in the late 1920's. Well-drilling surpassed lithopone in 1938 and has continued to exceed it ever since. Barium chemicals have required larger quantities of barite since the outbreak of World War II, but has always been in third place with respect to ground barite and lithopone. Flotation barite, though ground, is classed as crude for the purposes of the following table and is included in both the "ground" and "total" columns.

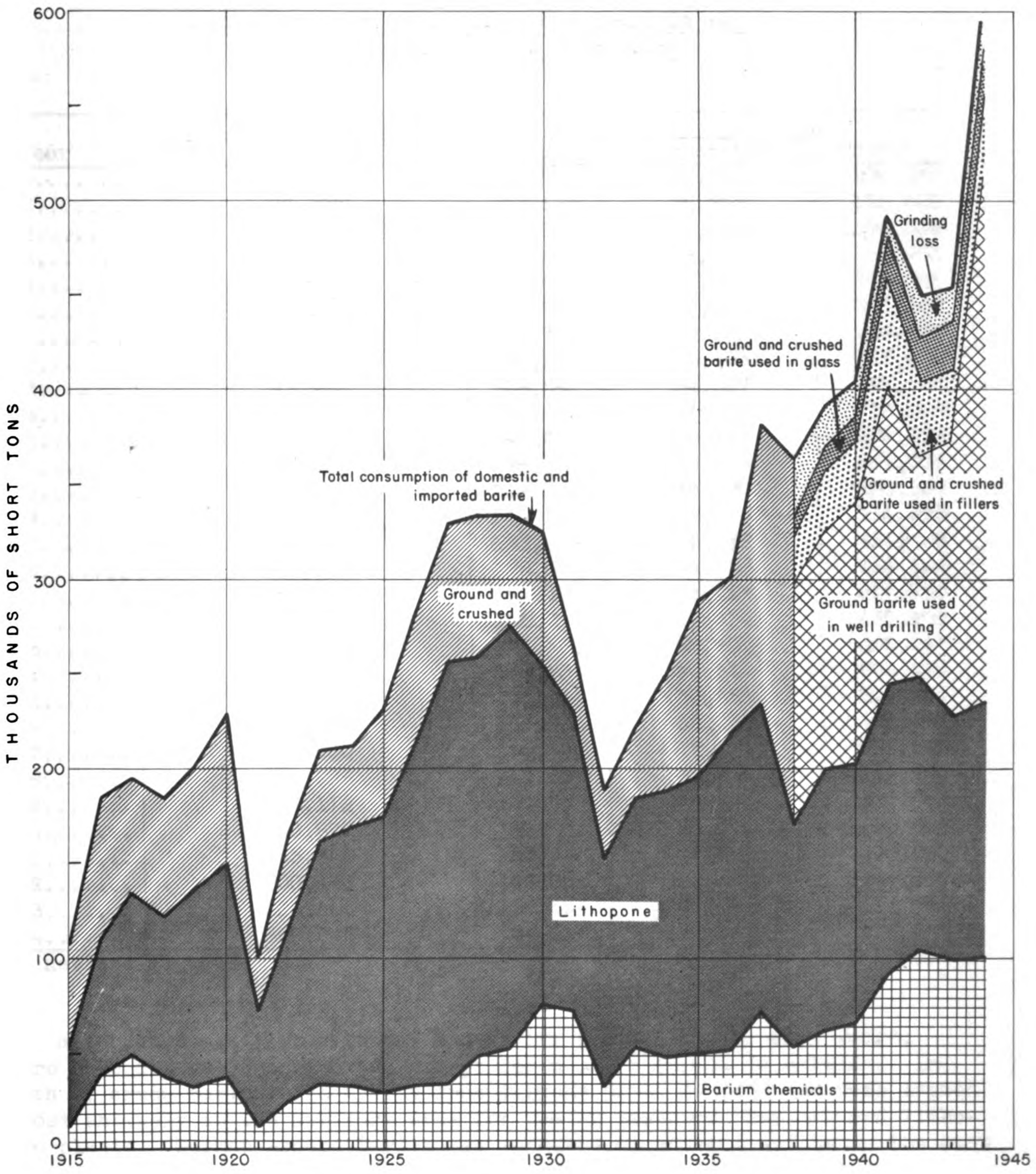

Figure 2. - Total consumption of domestic and imported barite in the United States, by industries, 1915-1944.

Crude barite (domestic and imported) used in the manufacture of ground barite and barium chemicals in the United States, 1915-44, short tons

Year	In manufacture of -			Total
	Ground and crushed barite	Lithopone	Barium chemicals	
1915.......	53,903	44,503	10,216	108,622
1916.......	75,507	71,898	38,283	185,688
1917.......	60,132	86,065	49,842	196,039
1918.......	62,440	85,282	38,041	185,763
1919.......	64,922	103,688	32,976	201,586
1920.......	79,052	113,181	37,210	229,443
1921.......	28,296	61,359	10,952	100,607
1922.......	48,280	94,259	25,303	167,842
1923.......	47,713	128,547	34,327	210,587
1924.......	42,855	137,127	33,181	213,163
1925.......	56,851	146,693	29,141	232,685
1926.......	69,048	178,889	33,119	281,056
1927.......	73,119	222,791	34,280	330,190
1928.......	74,814	211,592	48,289	334,695
1929.......	58,770	223,188	52,448	334,406
1930.......	69,426	178,944	76,825	325,195
1931.......	35,393	157,181	72,696	265,270
1932.......	36,402	120,378	32,629	189,409
1933.......	38,026	131,761	53,260	223,047
1934.......	61,123	140,734	48,619	250,476
1935.......	93,692	146,164	50,488	290,344
1936.......	83,990	167,014	52,445	303,449
1937.......	148,930	162,681	72,371	383,982
1938.......	193,728	117,007	54,250	364,985
1939.......	192,112	141,556	58,015	391,683
1940.......	200,899	136,885	66,604	404,388
1941.......	243,846	153,982	93,005	490,833
1942.......	200,443	144,821	104,160	449,424
1943.......	225,154	1/129,493	1/99,097	1/453,744
1944.......	360,045	134,597	100,921	595,563

1/ Revised figures.

Although domestic barite has had tariff protection for many years, there have always been imports, except for a short period in wartime. Imports of crude barite were mostly from Germany prior to 1939 and were landed almost entirely in the New York area for use in seaboard chemical and lithopone plants. German ground barite was received at several points on the east coast for use as filler. Some crude and ground barite also have been received from Cuba for use in well drilling. Nova Scotia (Canada) has supplied material for chemical and lithopone use in the Northeast. France, Spain, and Greece also have shipped barite to the United States. Although import statistics frequently show Netherlands as a source, such barite is really German shipped via Rotterdam.

Imports of barite for consumption in the United States, by countries, 1934-44

	1934		1935		1936		1937		1938		1939		1940		1941		1942		1943		1944	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
Crude barite:																						
Algeria	—	—	—	—	—	—	—	—	—	—	51	$161	—	—	—	—	—	—	—	—	—	—
Belgium	397	$2,847	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Brazil	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2	$25
Canada	—	—	—	—	—	—	—	—	—	—	1	7	—	—	—	—	4,088	$31,490	—	—	67,126	456,088
China	—	—	—	—	1	$14	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cuba	—	—	—	—	183	894	1,345	$6,298	6,367	$27,578	11,536	55,817	7,391	$41,342	456	$2,518	592	3,266	—	—	—	—
France	114	876	1,018	$5,073	5,040	27,000	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Germany	16,643	63,845	6,720	42,700	110	1,305	16,099	62,605	4,200	27,188	—	—	—	—	—	—	—	—	—	—	—	—
Greece	—	—	3	50	560	2,917	9,026	52,057	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Italy	56	352	—	—	1,213	4,400	204	1,832	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mexico	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	760	3,551
Netherlands	15,651	89,850	20,752	120,228	26,714	133,671	38,301	204,298	14,278	96,469	—	—	—	—	—	—	—	—	—	—	—	—
Spain	6,720	13,882	15,401	58,465	22	115	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Yugoslavia	—	—	—	—	—	—	17	134	—	—	—	—	—	—	—	—	—	—	—	—	—	—
U.S.S.R.	2	20	3,153	19,738	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
United Kingdom	448	3,265	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	40,031	174,937	47,047	246,254	53,843	170,316	64,992	327,224	24,845	151,235	11,588	55,985	7,391	41,342	456	2,518	4,680	34,756	—	—	67,888	459,664
Ground barite:																						
Algeria	—	—	—	—	—	—	—	—	—	—	28	$222	—	—	—	—	—	—	—	—	—	—
Canada	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	6,660	$176,287
Chile	—	—	—	—	—	—	3	$75	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cuba	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	5,304	67,630
Germany	287	$2,884	525	$6,926	1,302	$15,204	1,022	12,009	179	$2,301	78	1,023	—	—	—	—	—	—	—	—	—	—
Italy	1,576	14,032	2,829	21,840	1,571	13,193	2,288	22,962	1,521	13,165	1,484	13,754	314	$3,299	—	—	—	—	—	—	—	—
United Kingdom	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(1)	$27	—	—
	1,863	16,916	3,354	28,766	2,873	28,397	3,313	35,046	1,700	15,466	1,590	14,999	314	3,299	—	—	—	—	(1)	27	11,964	243,917
Witherite:																						
U.S.S.R.	66	$337	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
United Kingdom	2,292	42,971	2,634	$48,551	2,464	$44,475	4,556	$82,341	2,115	$43,568	3,819	$64,106	3,584	$70,126	4,790	$107,238	3,066	$60,824	448	$9,452	—	—
	2,358	43,808	2,634	48,551	2,464	44,475	4,556	82,341	2,115	43,568	3,819	64,106	3,584	70,126	4,790	107,238	3,066	60,824	448	9,452	—	—

1/ Less than one ton.

Before World War I, the production of barium chemicals in the United States was negligible, and imports, mainly from Germany, were a necessity. Several of the present barium chemical manufacturers obtained a footing during the first war, however, and by the beginning of the depression their output had largely displaced imports. Some chemicals, such as the nitrate and hydroxide, however, were imported regularly up until 1940. Imports of barium peroxide (dioxide) were curtailed abruptly in 1926 owing to the development of electrolytic methods of making hydrogen peroxide.

The domestic output of byproduct blanc fixe from this method of making hydrogen peroxide fell concomitantly, accounting for increased imports of blanc fixe until 1931. Most of the large imports of barium carbonate during the boom twenties were doubtless used to protect brick from scum.

Barium chemicals sold or used by producers in the United States, 1915-40[1]/[2]/

	Artificial barium carbonate (chemically precipitated)		Barium chloride		Blanc fixe (precipitated barium sulfate)		Other barium chemicals		Total	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
1915 ..	2,746	(3)	2,106	(3)	(4)	(3)	3,971	(3)	8,823	(3)
1916 ..	6,844	$343,582	3,643	$238,480	3,337	$167,404	2,968	$1,213,054	16,792	$1,962,520
1917 ..	8,238	(3)	4,870	(3)	6,314	(3)	3,081	(3)	22,503	(3)
1918 ..	7,661	369,099	4,530	324,437	9,522	426,354	1,473	474,365	23,186	1,594,255
1919[5]/.	7,135	400,193	4,509	330,442	5,227	257,344	3,142	531,809	20,013	1,519,788
1920 ..	7,484	573,670	3,084	313,712	8,046	431,323	2,146	419,929	20,760	1,743,634
1921 ..	1,956	158,929	(4)	(4)	2,471	180,130	1,060	73,216	5,487	412,275
1922 ..	2,281	163,636	2,022	163,749	7,349	516,686	2,249	407,608	13,901	1,251,679
1923 ..	6,362	441,471	3,301	270,333	6,761	490,479	379	29,363	16,803	1,231,646
1924 ..	6,038	411,332	3,859	297,182	7,796	464,152	441	41,234	18,154	1,213,900
1925 ..	4,962	279,346	(4)	(4)	11,748	792,036	1,944	136,388	18,654	1,207,770
1926 ..	5,394	298,121	4,592	279,510	(4)	(4)	11,925	747,631	21,911	1,325,262
1927 ..	5,969	313,613	3,708	213,446	13,395	876,842	871	114,093	23,943	1,517,994
1928 ..	7,626	416,227	5,224	301,490	(4)	(4)	21,119	1,327,439	33,969	2,045,156
1929 ..	7,902	450,041	6,545	412,902	(4)	(4)	23,991	1,603,362	38,438	2,466,305
1930 ..	5,224	260,284	(4)	(4)	(4)	(4)	26,139	1,495,243	31,363	1,755,527
1931 ..	5,687	253,189	(4)	(4)	31,151	1,827,713	7,341	628,261	44,179	2,709,163
1932 ..	3,295	149,869	3,955	240,843	14,454	933,068	623	126,836	22,327	1,450,616
1933 ..	3,810	181,857	(4)	(4)	30,744	1,197,131	5,539	356,970	40,093	1,735,958
1934 ..	4,706	245,315	(4)	(4)	18,115	1,084,733	7,084	601,346	29,905	1,931,394
1935 ..	7,329	357,585	(4)	(4)	18,067	980,191	7,520	642,576	32,916	1,980,352
1936 ..	11,347	515,624	(4)	(4)	16,149	890,310	8,393	698,942	36,389	2,104,876
1937 ..	10,755	511,357	(4)	(4)	28,250	1,614,764	8,632	796,988	47,637	2,923,109
1938 ..	9,543	459,901	(4)	(4)	19,428	921,203	10,963	723,896	39,934	2,110,000
1939 ..	12,478	617,799	(4)	(4)	18,653	898,198	9,858	814,170	40,989	2,330,167
1940 ..	13,339	616,331	(4)	(4)	22,247	1,250,303	10,813	803,886	46,399	2,670,520

1/ To avoid duplication, the barium chemicals reported here do not include the output of firms that make these chemicals from such products as barium chemicals and imported barite and witherite purchased in the open market. The totals of barium chemicals shown as sold or used during this period are therefore incomplete.

2/ Data for 1941-44 are shown in a following table.

3/ Data not available.

4/ Included under "Other barium chemicals."

5/ Figures cover production, not sales.

Barium chemicals produced and used or sold by producers in the United States, 1941-44, in short tons

Chemical	Plants	Produced	Used by producers in other barium chemicals[1]	Sold by producers[2]	
				Short tons	Value
Black ash:[3]					
1941	16	161,723	159,397	1,648	$65,350
1942	18	163,119	163,043	950	41,275
1943	18	148,179	147,975	553	23,969
1944	17	153,624	153,573	371	16,316
Carbonate (synthetic):					
1941	5	21,857	5,297	16,298	724,977
1942	7	[4]30,204	[4]14,724	14,905	830,034
1943	5	[4]35,308	[4]21,513	13,979	753,832
1944	5	37,911	27,551	9,313	467,288
Chloride (100 percent basis):					
1941	3	13,873	994	12,789	1,038,322
1942	3	13,439	1,722	11,497	913,290
1943	3	15,379	5,111	10,545	942,399
1944	3	17,183	5,766	11,446	955,571
Dioxide:					
1941	2	(5)	(5)	(5)	(5)
1942	2	(5)	(5)	(5)	(5)
1943	3	4,123	[4]1,682	[4]2,495	[4]563,756
1944	2	(5)	(5)	(5)	(5)
Hydroxide:					
1941	4	1,695	755	1,027	119,062
1942	3	2,327	66	2,335	267,572
1943	4	2,761	54	2,715	281,138
1944	3	2,462	98	2,429	244,072
Nitrate:					
1941	3	491	------	432	72,539
1942	5	11,547	------	[4]11,489	[4]2,262,061
1943	5	12,157	------	12,324	2,376,631
1944	3	11,160	------	11,333	2,066,976
Oxide:					
1941	2	(5)	(5)	(5)	(5)
1942	3	3,922	3,543	155	30,752
1943	3	5,189	4,998	170	37,925
1944	3	4,748	4,638	84	19,158
Sulfate (synthetic):					
1941[6]	7	25,509	15,427	11,302	668,084
1942[6]	6	22,965	14,562	8,226	506,183
1943[6]	7	23,811	10,628	13,646	873,312
1944	8	29,022	15,298	12,926	900,910
Other barium chemicals:					
1941	(7)	[4]30,460	4,782	[4]27,823	[4]3,118,841
1942[4]	(7)	25,881	1,803	21,053	2,554,603
1943[4]	(7)	21,399	-------	21,442	2,461,575
1944	(7)	28,414	2,904	25,568	3,070,027
Total:					
1941	[8]20	------	------	[4]71,319	[4]5,807,175
1942	[8]23	------	------	[4]70,610	[4]7,405,770
1943	[8]24	------	------	[4]77,869	[4]8,314,537
1944	[8]22	------	------	73,470	7,740,318

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[1] Includes purchased material. [2] Exclusive of purchased material and exclusive of sales by one producer to another. [3] Black-ash data include lithopone plants. [4] Revised figures. [5] Included under "Other barium chemicals." [6] Revised figures owing to expanded coverage. [7] Plants included in above figures. [8] A plant producing more than 1 product is counted but once in arriving at grand totals.

Barium chemicals imported for consumption in the United States, 1913-44 (Value at port of shipment)

Year	Barium dioxide		Blanc fixe (precipitated barium sulfate)		Barium carbonate (precipitated)		Barium chloride	
	Pounds	Value	Short tons	Value	Short tons	Value	Short tons	Value
1913..	4,173,188	$239,000	2,442	$62,785	2,043	$38,949	1,863	$37,620
1914..	5,741,752	332,709	1,424	32,619	1,533	28,221	2,961	68,866
1915..	2,397,359	218,776	721	18,501	143	2,786	1,281	31,295
1916..	106,863	6,590	338	17,810	-	-	3	608
1917..	-	-	115	3,333	54	1,554	-	-
1918..	-	-	-	-	-	-	-	-
1919..	-	-	(1)	90	4	2,666	550	19,846
1920..	501,673	64,447	165	8,485	476	37,462	1,595	151,778
1921..	1,337,972	127,631	769	22,470	2,238	80,603	2,186	72,621
1922..	2,018,194	189,334	2,187	76,445	5,212	210,250	1,962	112,785
1923..	1,810,000	152,270	587	32,063	1,901	79,482	1,278	75,014
1924..	1,720,000	120,374	1,047	50,465	3,752	128,217	2,330	100,810
1925..	1,270,000	70,553	1,996	81,439	7,188	160,164	2,167	67,306
1926..	98,000	8,157	2,973	136,697	9,224	189,167	1,773	49,426
1927..	12,000	1,264	2,400	107,179	4,918	119,014	1,577	45,285
1928..	12,000	1,310	3,680	168,923	5,222	116,241	1,172	25,253
1929..	133	21	3,501	168,367	3,206	69,236	78	3,049
1930..	222	28	2,994	133,260	2,662	52,427	7	372
1931..	122	11	930	38,083	1,110	20,839	6	201
1932..	328	27	656	24,100	303	5,630	39	1,208
1933..	2,000	82	245	12,093	49	1,632	6	526
1934..	370	58	459	26,156	-	-	107	4,808
1935..	450	72	141	9,403	11	631	392	17,170
1936..	1,392	223	123	6,971	30	889	244	10,355
1937..	229	34	109	7,617	30	848	315	13,761
1938..	100	13	106	5,102	(1)	32	69	2,351
1939..	350	51	38	1,891	-	-	39	1,329
1940..	-	-	-	-	-	-	-	-
1941..	4,032	208	15	865	-	-	-	-
1942..	40,992	2,119	28	1,357	-	-	36	15,770
1943..	-	-	-	-	-	-	18	7,885
1944..	-	-	-	-	-	-	-	-

1/ See footnotes at end of table on following page.

Barium chemicals imported for consumption in the United States, 1913-44 (Value at port of shipment) (Cont'd.)

Year	Barium nitrate		Barium hydroxide		Barium oxide		Barium compounds (n.e.s.)	
	Short tons	Value	Short tons	Value	Pounds	Value	Short tons	Value
1922	2/179	$16,795	2/73	$6,573	(3)	(3)	(4)	(4)
1923	511	59,766	181	16,872	(3)	(3)	(4)	(4)
1924	513	54,638	174	8,241	(3)	(3)	(4)	(4)
1925	703	58,192	120	5,605	(3)	(3)	(4)	(4)
1926	602	49,494	236	9,789	(3)	(3)	(4)	(4)
1927	711	65,284	222	12,439	(3)	(3)	(4)	(4)
1928	789	69,010	186	10,031	(3)	(3)	(4)	(4)
1929	615	56,770	202	11,809	(3)	(3)	(4)	(4)
1930	407	31,985	220	12,235	(3)	(3)	(4)	(4)
1931	423	29,796	345	25,570	242,000	$18,870	(4)	(4)
1932	330	21,421	235	10,494	22	11	(4)	(4)
1933	359	31,140	281	15,542	220,000	9,416	8	$3,224
1934	454	44,884	287	17,548	132	66	4	1,266
1935	258	24,412	271	16,987	33	26	8	1,852
1936	185	19,107	370	25,423	287	155	8	2,231
1937	157	15,836	310	21,004	298	161	28	6,455
1938	126	12,061	236	16,874	-	-	50	11,320
1939	100	11,094	360	19,975	22	13	27	7,244
1940	18	1,427	151	3,332	-	-	22	4,286
1941	-	-	292	10,791	-	-	8	4,071
1942	(5)	1	147	9,361	-	-	154	76,667
1943	-	-	151	9,850	-	-	43	15,385
1944	-	-	95	7,382	-	-	-	-

1/ Less than a ton.
2/ Sept. 22 to Dec. 31. Not separately recorded prior to 1922.
3/ Not separately recorded prior to 1931.
4/ Not separately recorded prior to 1933.
5/ 53 pounds.

Lithopone[1] sold or used by producers in the United States, 1906-44

Year	Sold or used by producers	
	Short tons	Value
1906	5,149	(2)
1907	10,275	$750,350
1908	8,292	639,483
1909	14,847	1,105,281
1910	12,655	916,512
1911	16,866	1,243,108
1912	24,220	1,702,119
1913	29,685	2,170,445
1914	32,819	2,490,530
1915	46,494	3,760,472
1916	51,291	5,798,927
1917	63,713	7,406,896
1918	62,403	7,923,276
1919	78,365	10,218,850
1920	89,373	12,484,925
1921	55,016	6,681,563
1922	83,360	9,214,040
1923	98,199	11,608,443
1924	109,469	12,531,397
1925	145,019	15,186,147
1926	159,931	16,062,197
1927	176,994	17,163,620
1928	200,468	19,073,914
1929	206,315	19,773,864
1930	164,065	15,897,683
1931	151,850	12,999,590
1932	121,667	10,176,856
1933	140,831	11,751,500
1934	145,565	12,235,624
1935	159,486	13,470,274
1936	158,319	12,976,754
1937	154,771	12,069,790
1938	125,746	9,975,012
1939	142,759	10,461,102
1940	151,802	10,197,897
1941	176,642	12,550,193
1942	137,320	10,828,924
1943	135,723	10,745,305
1944	142,905	11,208,891

[1] Exclusive of cadmium lithopone.

[2] Data not available.

Lithopone[1] sold or used by producers, 1927-44, by consuming industries

Year	Paints, enamels, and lacquers	Floor coverings and textiles	Rubber	Other	Total
1927.................	131,145	31,186	7,653	7,010	176,994
1928.................	149,122	35,416	6,898	9,032	200,468
1929.................	150,804	37,506	7,176	10,829	206,315
1930.................	126,076	23,656	5,997	8,336	164,065
1931.................	119,446	20,780	5,833	5,791	151,850
1932.................	93,465	17,601	3,955	6,646	121,667
1933.................	106,995	18,472	5,078	10,286	140,831
1934.................	114,472	14,811	4,596	11,686	145,565
1935.................	124,615	19,440	4,435	10,996	159,486
1936.................	122,461	23,085	4,908	7,865	158,319
1937.................	122,915	20,194	4,383	7,279	154,771
1938.................	101,924	15,400	3,148	5,274	125,746
1939.................	113,995	17,429	3,189	8,146	142,759
1940.................	117,075	18,738	3,387	12,602	151,802
1941.................	132,691	21,114	3,547	19,290	176,642
1942.................	109,216	15,775	1,047	11,282	137,320
1943.................	103,860	15,999	1,078	14,786	135,723
1944.................	108,800	14,746	726	18,633	142,905

[1] Exclusive of cadmium lithopone.

Lithopone imported for consumption into the United States, 1913-44 1/

Year	Short tons	Value	Average	Year	Short tons	Value	Average
1913..	2,363	$146,474	$61.99	1929..	8,409	$725,554	$86.28
1914..	3,990	271,310	68.00	1930..	7,018	595,597	84.87
1915..	2,044	137,816	67.42	1931..	5,674	428,523	75.52
1916..	2,341	405,730	173.31	1932..	4,724	271,678	57.51
1917..	224	29,199	130.35	1933..	5,596	313,341	55.99
1918..	-	-	-	1934..	3,927	219,752	55.96
1919..	739	122,708	166.05	1935..	4,603	256,731	55.77
1920..	1,714	263,240	153.58	1936..	4,781	273,571	57.22
1921..	5,247	432,019	82.34	1937..	5,601	302,417	53.99
1922..	10,763	885,671	82.29	1938..	3,932	207,121	52.68
1923..	10,440	776,383	74.37	1939..	2,641	130,893	49.56
1924..	6,830	543,025	79.51	1940..	-	-	-
1925..	6,330	478,395	75.58	1941..	(2)	9	-
1926..	8,686	661,700	76.18	1942..	-	-	-
1927..	7,979	656,166	82.24	1943..	-	-	-
1928..	9,885	808,200	81.76	1944..	-	-	-

1/ Not separately recorded prior to 1913.
2/ 112 pounds.

Lithopone exported from the United States, 1922-44 1/

Year	Short tons	Value	Average	Year	Short tons	Value	Average
1922..	1,616	$169,982	$105.19	1934..	2,401	$199,508	$83.09
1923..	1,485	176,624	118.94	1935..	2,372	221,611	93.43
1924..	923	104,783	113.52	1936..	2,538	229,942	90.60
1925..	1,287	132,771	103.16	1937..	2,671	231,622	86.72
1926..	1,941	200,412	103.25	1938..	1,734	153,567	88.56
1927..	2,110	222,585	105.49	1939..	4,845	392,798	81.07
1928..	3,326	337,565	101.49	1940..	14,298	1,112,362	77.80
1929..	4,556	463,235	101.68	1941..	21,527	2,079,229	96.59
1930..	3,665	380,047	103.70	1942..	17,036	1,733,698	101.77
1931..	3,821	341,257	89.31	1943..	17,320	1,637,217	94.53
1932..	3,212	270,195	84.12	1944..	11,551	1,106,430	95.79
1933..	1,186	107,923	91.00				

1/ Not separately recorded prior to 1922.

MARKET DIRECTORY

A. Producers of crude barite and witherite in the United States in 1944.

(Producers of less than 1,000 short tons are not included.)

Name and address	Mine or mill location (nearest town)	Method of recovery
ARKANSAS:		
Baroid Sales Division, National Lead Co., 830 Ducommun St., Los Angeles, Calif.	Malvern	Flotation.
Magnet Cove Barium Corp., Malvern	do.	Do.
CALIFORNIA:		
Baroid Sales Division, National Lead Co., 830 Ducommun St., Los Angeles	El Portal	Shot from veins. (Barite and witherite)
Industrial Minerals & Chemical Co., 6th and Gilman Sts., Berkeley	Washington	Shot from veins.
GEORGIA:		
Barytes Mining Co., Box 224, Cartersville	Cartersville	Washer.
Dellinger, Brown, & Duckett, Cartersville	do.	Do.
T. E. Johnsey, Cartersville	do.	Do.
New Riverside Ochre Co., Cartersville	do.	Do.
Paga Mining Co., Cartersville	do.	Do.
George E. Shropshire, Cartersville	do.	Do.
L. A. Wood Co., Sweetwater, Tenn.	do.	Do.
MISSOURI:		
Cadet Mining Co., Cadet	Cadet	Do.
Campbell Bros., Russellville	Cole Camp	Do.
Do.	Russellville	Do.
J. E. Carter Mining Co., Potosi	Potosi	Do.
Cordia Mining Co., Potosi	Mineral Point	Do.
De Soto Mining Co., De Soto	Richwoods	Do.
H. & P. Mining Co., Potosi	Old Mines	Do.
Hanenkratt Gravel Co., 5202 Brookwood St., Kansas City	Linn Creek	Do.
Fred Hornsey & Co., Potosi	Potosi	Do.
M. & B. Mining Co., Potosi	Old Mines	Hand-mined.
Midwest Mining Co., Box 87, Potosi	Richwoods	Washer.
Ozark Products Co., Box 190, Potosi	Cadet	Do.
Lloyd Sestak, Henley	Henley	Do.
Superior Mineral Co., Cadet	Cadet	Do.
Do.	Richwoods	Do.
Whaley & Scott Mining Co., Box 111, De Soto	do.	Do.
Xact Clays, Inc., Box 306, Potosi	Potosi	Do.
NEVADA:		
Barium Products, Ltd., Newark, Calif.	Battle Mountain	Shot from veins.
California-Nevada Barytes Mines Division of The Glidden Co., 766 50th Ave., Oakland, Calif.	do.	Do.

A. Producers of crude barite and witherite in the United States in 1944 (Producers of less than 1,000 short tons are not included.) (Cont'd.)

Name and address	Mine or mill location (nearest town)	Method of recovery
SOUTH CAROLINA:		
Clinchfield Sand & Feldspar Corp., 618 Mercantile Trust Bldg., Baltimore 2, Md.	Kings Creek	Shot from veins.
TENNESSEE:		
Clinchfield Sand & Feldspar Corp., 618 Mercantile Trust Bldg., Baltimore 2, Md.	Del Rio	Do.
Sweetwater Mining Co., Sweetwater	Sweetwater	Washer.
Wolf River Corp., Jamestown	do.	Do.
L. A. Wood Co., Sweetwater	do.	Do.
R. E. Wood, Sweetwater	do.	Do.

B. Barite grinders (possible buyers of crude barite)

The Glidden Co., Chemical & Pigment Division, 766 50th Ave., Oakland 1, Calif.
Baroid Sales Division, National Lead Co., 830 Ducommun St., Los Angeles 12, Calif.: plants at Fountain Farm, Mo., El Portal, Calif., and Malvern, Ark.
Clinchfield Sand & Feldspar Corp., 618 Mercantile Trust Bldg., Baltimore 2, Md.
De Lore Division, National Lead Co., P. O. Box 2808, Carondelet Station, St. Louis 11, Mo.
Eversole Maclay, Mineral Point, Mo.
Barium Products, Ltd., Newark, Calif.
Industrial Minerals & Chemical Co., 6th and Gilman Sts., Berkeley, Calif.
Magnet Cove Barium Corp., Malvern, Ark.
Geo. S. Mepham Corp., Ayers & Lodge Sts., East St. Louis, Ill.
New Riverside Ochre Co., Cartersville, Ga.
F. E. Schundler & Co., Inc., 504 Railroad St., Joliet, Ill., and Long Island City, N. Y.
Southwark Manufacturing Co., Camden, N. J.
Thompson, Weinman & Co., Cartersville, Ga.
L. A. Wood, Sweetwater, Tenn. (Makes crushed barite only.)

C. Manufacturers of Barium Chemicals in 1944. (Possible buyers of crude barite are starred.)

Barium & Chemicals, Inc., Dept. A, Willoughby, Ohio.
Barium hydroxide and oxide.

*Barium Products, Ltd., Newark, Calif. Plant: Modesto, Calif.
Barium carbonate, dioxide, hydroxide, oxide, and sulfate.

*Barium Reduction Corp., Drawer 1, South Charleston, West Va.
Barium carbonate, chloride, dioxide, hydroxide, oxide, and sulfate.

*Baroid Sales Division, National Lead Co., 830 Ducommun St., Los Angeles 12, Calif.
Plant: Fountain Farm, Mo. Black ash.

H. C. Bugbird Co., Inc., Carlstadt, N. J.
Barium nitrate.

*Chemical Products, Cartersville, Ga.
Barium carbonate, chloride, and chromate.

*Chicago Copper & Chemical Co., Blue Island, Ill.
Barium carbonate and nitrate.

*E. I. duPont de Nemours & Co., Wilmington 98, Del.
Plant: Grasselli, N. J. Barium chloride.
Plant: Newport, Del. Barium sulfate.

Eastman Kodak Co., Kodak Park Works, 1669 Lake Ave., Rochester 4, N. Y.
Barium sulfate.

*Mallinckrodt Chemical Works, St. Louis, Mo.
Barium sulfate.

*National Lead Co., Titanium Division, 111 Broadway, New York, N. Y.
Plant: St. Louis County, Mo. Barium carbonate and sulfate.

*Standard Ultramarine Co., Huntington 18, W. Va.
Barium sulfate.

Westvaco Chlorine Products Corp., Carteret, N. J.
Barium nitrate and sulfate.

D. Manufacturers of lithopone. (Possible buyers of crude barite.)

Eagle-Picher Lead Co., American Bldg., Cincinnati, Ohio. Plant: Argo, Ill.
E. I. duPont de Nemours & Co., Wilmington 98, Del. Plant: Newport, Del.
The Glidden Co., Chemical and Pigment Division, 766 50th Ave., Oakland 1, Calif.
The Glidden Co., Chemical & Pigment Division, St. Helena, Baltimore 22, Md.
The Glidden Co., Chemical & Pigment Co., Inc., P. O. Box 191, Collinsville, Ill.
The New Jersey Zinc Co., Mineral Point Zinc Division, 160 Front St., New York 7, N. Y. Plant: Depue, Ill.
New Jersey Zinc Co. of Pennsylvania, 160 Front St., New York 7, N. Y.
Ozark Smelting & Mining Co., 101 Prospect Ave., N. W., Cleveland 1, Ohio. Plant: Coffeyville, Kans.

E. Buyers of ground barite for use in oil-well drilling.
(Such buyers are numbered in the thousands.)

Lists of well drillers are given in such compilations as Petroleum Register, Palmer Publications, 412 West Sixth St., Los Angeles 14, Calif. ($10).

F. Possible buyers of crushed or ground barite for use in glass.

Anchor-Hocking Glass Co., 109 N. Broad St., Lancaster, Ohio.
Armstrong Cork Co., Lancaster, Pa.
Ball Bros., Ryan and Burt Sts., Muncie, Ind.
Brockway Glass Co., Brockway, Pa.
Buck Glass Co., Fort and Silica Sts., Baltimore, Md.
Carr-Lowrey Glass Co., Baltimore, Md.
Commercial Glass Co., Fairmont, W. Va.
Demuth Glass Co., Parkersburg, W. Va.
Diamond Glass Co., Royersford, Pa.
Fairmont Glass Works, Keystone Ave. and Belt Ry., Indianapolis, Ind.
Foster-Forbes Glass Co., Marion, Ind.
Glenshaw Glass Co., Glenshaw, Pa.
Hazel-Atlas Glass Co., 1942 Danneburg St., Wheeling W. Va.
Imperial Glass Co., Bellaire, Ohio.
Jeannette Glass Co., Jeannette, Pa.
A. H. Kerr & Co., Sand Springs, Okla.
Kimble Glass Co., Vineland, N. J.
Latchford-Marble Glass Co., P. O. Box 4707, Los Angeles, Calif.
McKee Glass Co., Jeannette, Pa.
Owens-Illinois Glass Co., Duraglas Bldg., Toledo, Ohio.
Owens-Illinois-Pacific Coast Co., 135 Stockton St., San Francisco, Calif.
Phoenix Glass Co., Monaca, Pa.
Pierce Glass Co., Port Allegany, Pa.
F. E. Reed Glass Co., Rochester, N. Y.
Sinclair Glass Co., Ceredo, W. Va.
Sterling Glass Co., Lapel, Ind.
Thatcher Manufacturing Co., Elmira, N. Y.
Vitro-Agate Co., Parkersburg, W. Va.

G. Possible buyers of ground barite for use in paint.

Alsamite Paint & Varnish Co., 3310 E. Thompson St., Philadelphia, Pa.
Amalgamated Paint Co., Inc., Pier 11, North River, New York, N. Y.
American Home Paint, Inc., 405 Watkins St., Brooklyn, N. Y.
Armstrong Cork Co., 1010 Concord St., Lancaster, Pa.
Atlantic Paint & Varnish Works, Wilmington, N. C.
Baker Paint & Varnish Co., 224 Suydam Ave., Jersey City, N. J.
E. S. Browning Co., 1515 Third St., San Francisco, Calif.
M. A. Bruder & Sons, 52nd and Grays Aves., Philadelphia 43, Pa.
C. E. Butler Co., 2868 Hanna St., Oakland 8, Calif.
Calbar Paint & Varnish Co., 2620 North Martha St., Philadelphia 25, Pa.
Central Paint & Varnish Works, 69 Prospect St., Brooklyn 1, N. Y.
Chilton Paint Co., 109 15th Ave., College Point, N. Y.
Clement Coverall Co., 615 Van Hook St., Camden, N. J.
H. B. Davies Co., 700 N. 275th St., Camden, N. J.
Durable Paint Co., 373 Hamilton Ave., Brooklyn, N. Y.
Fisher Thorsen & Co., Inc., 2100 N. W. 22nd Ave., Portland 10, Oreg.
Ford Motor Co., Dearborn, Mich.
W. P. Fuller & Co., Portland, Oreg.

W. P. Fuller & Co., 301 Mission St., San Francisco, Calif.
General Paint Corp., 2627 Army St., San Francisco 19, Calif.
M. Grumbacker, 460 W. 34th St., New York 1, N. Y.
Hock Paint & Chemical Works, Phoenixville, Pa.
R. M. Hollingshead Corp., 840 Cooper St., Camden, N. J.
C. H. Howell & Co., 212 Race St., Philadelphia, Pa.
Impervious Paint & Varnish Co., 448 North 10th St., Philadelphia, Pa.
Irwin Paint Co., Fourth and Addison, Berkeley, Calif.
Jaegle Paint & Varnish Co., 1607 South 20th St., Philadelphia, Pa.
Landets-Segal Color Co., 78 Delevan St., Brooklyn, N. Y.
Leland Moore Paint & Oil Co., Charleston, S. C.
Longview Paint & Varnish Co., Longview, Wash.
R. N. Nason & Co., 151 Potrero Ave., San Francisco, Calif.
Payson Paint & Varnish Co., 804 E. 141st St., New York, N. Y.
Peerless Paint & Varnish Corp., 26 Court St., Brooklyn, N. Y.
T. J. Ronan Co., 749 E. 135th St., New York 54, N. Y.
Roxalin Flexible Finishes, 800 Magnolia Ave., Elizabeth, N. J.
Gilbert Spruance Co., Richmond & Tioga Sts., Philadelphia 34, Pa.
Stay & Day Paint Materials, 2530 E. 14th St., Los Angeles, Calif.
Tri-City Paint Co., 1220 Fourth St., Berkeley 2, Calif.
Paul Uhlich & Co., 90 West St., New York, N. Y.
United Color & Pigment Co., Inc., Newark, N. J.
U. S. Gypsum Co., 300 W. Adams St., Chicago, Ill.
U. S. Kalsomine Co., 50 Church St., New York, N. Y.
Utility Color Co., 377 Frelinghuysen Ave., Newark, N. J.
Wesco Waterpaints, 5th and Grayson St., Berkeley 2, Calif.

H. Possible buyers of ground barite for use in rubber.

Armstrong Cork Co., Lancaster, Pa.
Atlantic Tubing & Rubber Co., 1756 Cranston St., Providence, R. I.
Bowling Green Rubber Co., Hoag and Prospect Sts., Toledo 6, Ohio.
Buckeye Reliner Producing Co., Lima, Ohio.
Castle Rubber Co., East Butler, Pa.
Firestone Tire & Rubber Co., Akron, Ohio.
General Asbestos & Rubber Co., North Charleston, S. C.
Hamilton Rubber Manufacturing Co., Mead and South Sts., Trenton, N. J.
R. M. Hollingshead Corp., Camden, N. J.
Ideal Rubber Co., 273 van Sinderen Ave., Brooklyn, N. Y.
Johns-Manville Co., Manville, N. J.
Laurie Rubber Reclaiming Co., New Brunswick, N. J.
Linear Packing & Rubber Co., 6464 State Road, Philadelphia, Pa.
Manhattan Rubber Division of Raybestos-Manhattan, Inc., Passaic, N. J.
Martin Rubber Co., Long Branch, N. J.
Okonite Co., Passaic, N. J.
Quaker Rubber Co., 4915 Comly St., Philadelphia 24, Pa.
Seiberling Rubber Co., Akron, Ohio.
U. S. Asbestos Division, Raybestos-Manhattan, Inc., Manheim, Pa.
U. S. Rubber Co., 1232 Sixth Ave., New York 20, N. Y.
Whitehead Bros. Rubber Co., 492 Whitehead Road, Trenton, N. J.

I. Possible buyers of ground barite for miscellaneous filler uses

Bar-Ray Products, Inc., 209 25th St., Brooklyn, N. Y.
Columbia Recording Corp., 1473 Barnum Ave., Bridgeport, Conn.
Durite Plastics, Inc., 5000 Summerdale Ave., Philadelphia, Pa.
Gulf Oil Corporation, Port Arthur, Tex.
Higgins Ink Co., Inc., 244 8th St., Brooklyn 15, N. Y.
Icard Cordage Co., Icard, N. C.
Joliet Wallpaper Mills, Inc., Joliet, Ill.
Keasbey & Mattison Co., Ambler, Pa.
Kienle & Co., 33 Nassau Ave., Brooklyn 22, N. Y.
Laclede-Christy Clay Products Co., St. Louis, Mo.
Landers Corporation, 837 Willis St., Toledo, Ohio.
Mannington Mills, Salem, N. J.
Minnesota Mining & Manufacturing Co., 900 Fauquier Ave., St. Paul, Minn.
Newport News Shipbuilding Co., Newport News, Va.
Quaker Chemical Products Co., Conshohocken, Pa.
C. Schrack & Co., 4th and Quarry Sts., Philadelphia, Pa.
Security Banknote Co., 55th & Sansom Sts., Philadelphia 39, Pa.
Swan Rubber Co., Bucyrus, Ohio.
Thermoid Co., 400 Whitehead Road, Trenton, N. J.
Tymstone Studio, 4056 South Princeton Ave., Chicago 9, Ill.
Fred M. Williams Co., 1288 Prospect Ave., Brooklyn 18, N. Y.

J. Possible buyers of ground and crushed barite for resale.

L. H. Butcher Co., 1504 N. W. Johnson St., Portland, Oreg.
L. H. Butcher Co., 2034 Bay St., Los Angeles 21, Calif.
L. H. Butcher Co., 15th and Vermont Sts., San Francisco, Calif.
L. H. Butcher Co., 1703 Sixth Ave., South, Seattle, Wash.
The O. Hommel Co., 209 Fourth Ave., Pittsburgh 30, Pa.
Charles Ingram & Co., Keyser Bldg., Baltimore 2, Md.
Miller & Zehrung Chemical Co., 1301 N. W. 12th Ave., Portland, Oreg.
Geo. A. Rowley Co., 937 North Front St., Philadelphia 23, Pa.
H. M. Royal, Inc., Trenton, N. J.
H. S. Stoller, Akron 8, Ohio.
Van Waters & Rogers, Inc., 2133 N. W. York St., Portland, Oreg.